American Cancer Society Institutional Research Grant No. IN-147F, Maryland Cancer Program/University of Maryland.

**Registry No.** (*Z*)-**1d-7e**, 124267-35-2; (*E*)-**1d-7e**, 124267-36-3; **2a**, 22117-97-1; **2b**, 23074-59-1; **2d-5b**, 124267-27-2; (*Z*)-**2d-7e**, 124267-33-0; (*E*)-**2d-7e**, 124267-34-1; **3**, 124267-24-9; **4b**, 124267-25-0; **5a**, 121590-82-7; **5b**, 124267-26-1; **5c**, 89998-56-1; (*Z*)-**6a**, 121590-83-8; (*E*)-**6a**, 75283-44-2; (*Z*)-**6b**, 121590-84-9; (*E*)-**6b**, 121590-89-4; (*Z*)-**6c**, 121590-85-0; (*E*)-**6c**, 121590-90-7; (*Z*)-**6e**, 121590-86-1; (*E*)-**6e**, 121590-91-8; (*Z*)-**6f**, 121590-87-2; (*E*)-**6f**, 111303-28-7; (*Z*)-**6g**, 124267-28-3; (*E*)-**6g**, 124267-29-4; (*Z*)-**6h**, 121590-88-3; (*E*)-**6h**, 121590-92-9; (*Z*)-**7a**, 29179-04-2; (*E*)-7a, 29179-03-1; (*Z*)-**7e**, 124267-31-8; (*E*)-**7e**, 124267-32-9; (*Z*)-**8a**, 124267-37-4; (*E*)-**8a**, 124267-38-5; (*Z*)-**8c**, 124267-39-6; (*E*)-**8c**, 124267-40-9; (*Z*)-**8d**, 124267-41-0; (*E*)-**8d**, 124267-42-1; (*Z*)-**8e**, 124267-43-2; (*E*)-**8e**, 124267-44-3; (*Z*)-**8f**, 124267-45-4; (*Z*)-**8g**, 124267-46-5; (*E*)-**8g**, 124267-47-6; **13a**, 124267-49-8; **13d**, 124267-50-1; **14a**, 124267-51-2; **14d**, 124267-52-3; TMSC≡CH, 1066-54-2; $Me_2CuLi$, 15681-48-8; MeCu(CN)Li, 41753-78-0; $Me_2Cu(CN)Li_2$, 80473-70-7; EtCu(CN)MgBr, 124267-54-5; $Et_2Cu(CN)(MgBr)_2$, 121589-72-8; $i\text{-}Pr_2Cu(CN)(MgCl)_2$, 121589-74-0; $Bu_2CuLi$, 24406-16-4; $Bu_2Cu(CN)(MgBr)_2$, 124267-55-6; $Bu_2Cu(CN)Li_2$, 80473-69-4; $t\text{-}Bu_2CuLi$, 23402-75-7; $t\text{-}Bu_2Cu(CN)Li_2$, 87263-84-1; $Ph_2CuMgBr$, 58938-91-3; $Ph_2CuMgBr{\cdot}Me_2S$, 124267-57-8; $Ph_2Cu(CN)(MgBr)_2$, 121589-76-2; $Ph_2Cu(CN)Li_2$, 80473-66-1; $(CH_2{=}CH)_2CuMgBr{\cdot}Me_2S$, 124267-59-0; $(CH_2{=}CH)_2Cu(CN)(MgBr)_2$, 113153-17-6; $(CH_2{=}CH)_2Cu(CN)Li_2$, 80473-65-0; PhSLi, 2973-86-6; 3-(1,3-butadienyl)-2-methyl-2-cyclopenten-1-one 2,4-dinitrophenylhydrazone, 124267-30-7; 3-(1,3-butadienyl)-2-methyl-2-cyclohexen-1-one 2,4-dinitrophenylhydrazone, 124267-48-7.

# Preparation of Allylic Acetates from Simple Alkenes by Palladium(II)-Catalyzed Acetoxylation

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The scope and limitations of palladium-catalyzed allylic acetoxylation of alkenes has been investigated, using benzoquinone–manganese dioxide as the reoxidation system. Unsubstituted cycloalkenes gave good to excellent yields of allylic acetates. Total yields were also good for many substituted cycloalkenes and for linear alkenes, but these substrates generally gave several isomeric acetates. The exploratory mechanistic studies show that the acetoxylation can proceed via both 1,2-acetoxypalladation and $\eta^3$-allylpalladium complex formation. The keen balance between these processes depends on the structure of the alkene.

## Introduction

Allylic acetates have become important intermediates in organic synthesis, in particular after it was realized that metal-catalyzed replacement of the acetoxy group by nucleophiles is a facile and efficient reaction.[1] Allylic acetates are usually prepared from the corresponding allylic alcohols, but a number of routes which lead directly from alkenes have been devised. Most of these involve peroxides[2] and/or a variety of metal salts.[3] Due to several factors, such as the necessity for stoichiometric amounts of metal reagents and lack of generality, these reactions have not been used extensively in organic synthesis.

We have recently shown that simple cycloalkenes may be efficiently and selectively converted into allylic acetates, using palladium acetate as catalyst in combination with an oxidation system consisting of benzoquinone and manganese dioxide (Scheme I).[4] In this paper we report on an examination of the scope of this reaction and also on the results of an exploratory study of its mechanism.

## Results and Discussion

In order to examine the generality of palladium-catalyzed allylic acetoxylation we have studied a range of olefins (Tables I and II). The reactions were performed in acetic acid solution, using 5% palladium acetate as catalyst, ca. 20% benzoquinone as cooxidant, and 110–200% manganese dioxide as oxidant. For a few alkenes, other ratios between substrate and catalyst were also

**Scheme I**


**1** n = 1 **4** n = 4
**2** n = 2 **5** n = 6
**3** n = 3 **6** n = 8

studied. The reaction temperature was generally 60 °C, but temperatures as low as room temperature were also used in some cases.

With the exception of cyclooctene, the unsubstituted cycloalkenes gave good yields of allylic acetates (Table I). This is also true for most of the substituted cycloalkenes (Table II) and for the two linear alkenes that were studied, (*E*)-3-hexene and (*E*)-5-decene (Table I).

There are considerable differences in reactivity among the substrates. Cyclopentene, cyclohexene, cycloheptene, and (*E*)-cyclododecene all reacted within 50 h or less at 60 °C to give good yields of allylic acetates (Table I, entries 1, 2, 4, and 7). In contrast, (*Z*)-cyclooctene and (*Z*)-

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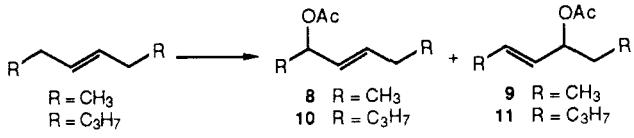
(1) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer Verlag: Heidelberg, 1980. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 8, pp 799–938. (c) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (d) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901–1930.
(2) Rawlinson, D. J.; Sosnovsky, G. *Synthesis* **1972**, 1–28.
(3) For reviews, see: (a) Muzart, J. *Bull. Soc. Chim. Fr.* **1986**, 65–77. (b) Rawlinson, D. J.; Sosnovsky, G. *Synthesis* **1973**, 567–603.
(4) (a) Heumann, A.; Akermark, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 453–454. (b) Heumann, A.; Hansson, S.; Rein, T.; Åkermark, B. *Org. Synth.*, in press.

0022-3263/90/1955-0975$02.50/0 

**Scheme II**




cyclodecene reacted very slowly, the latter requiring 12 days at 60 °C for ca. 90% conversion (Table I, entries 5 and 6). The reasons for the striking differences in reactivity are not clear. It is tempting to suggest that conformational factors in the intermediate $\eta^2$-complexes (or possibly $\eta^3$-allyl complexes) of the 8- and 10-membered ring substrates are the cause.[5]

Also the reactivities of the desired allylic acetates are of importance, and low yields were in many cases correlated with further oxidation to diacetates. In this context it is interesting to compare cyclooctene and cyclodecene. Cyclooctene gave only 35% optimized yield of the allylic acetate after 90 h at 60 °C, while cyclodecene, although the reaction was not complete even after 12 days, gave essentially quantitative yield of allylic acetate, based on consumed cycloalkene (Table I, entries 5 and 6). The major byproducts in the oxidation of cyclooctene were diacetates, suggesting that in this particular case the primary product is about as reactive as the starting material.

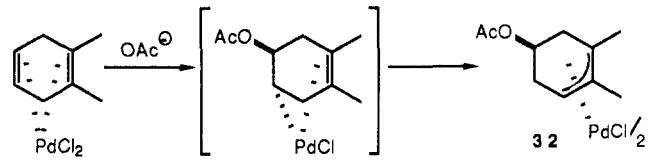
The configuration around the double bond, *E* or *Z*, is important, but its influence has only been studied fortuitously. Commercial cyclododecene, which was used in our oxidation reactions, contains ca. 60% *E* and 30% *Z* isomer, the remainder being mainly cyclododecane. After about 80% conversion (43 h at 60 °C), 93% of the (*E*)-cyclododecene and only 67% of the *Z* isomer have been consumed.[6] This is probably the result of an interplay between factors such as intrinsic reactivity of *E* and *Z* double bonds, coordinating ability, and conformational factors. The relative importance of these factors has to be studied separately.

An observation, that was not anticipated, is that cyclopentene and *cis*-bicyclo[3.3.0]oct-2-ene were very reactive substrates, while indene reacted very sluggishly[7] (Table I, entry 1; Table II, entries 2 and 3).

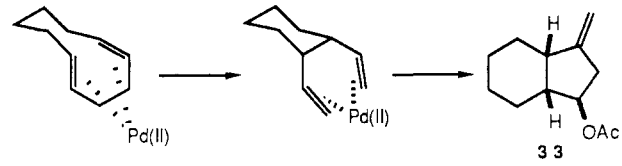
The two linear alkenes (*E*)-3-hexene and (*E*)-5-decene both reacted at a rate comparable to that of the cycloalkenes. A 1:1 mixture of two acetates was formed in both cases (Scheme II; table I, entries 9 and 10). The products from (*E*)-3-hexene were identified as **8** and **9**, but with those from (*E*)-5-decene the assignments as **10** and **11** are tentative.

In these reactions it was noted that although benzoquinone is generally necessary for a smooth oxidation it also slows down the rate. The reason is probably competition between the alkene and benzoquinone for palladium(II). Thus, the rate of reaction of (*E*)-3-hexene in the presence of 200% benzoquinone is much lower than that obtained with the combination of 20% benzoquinone and 120% manganese dioxide. With alkenes such as cyclohexene, which probably coordinate more efficiently to palladium(II), the effects of the benzoquinone concentration on the rate were smaller.

**Scheme III**




**Scheme IV**




Since one important factor is the coordinating power of the alkenes, it seemed probable that polyenes would be more reactive than the corresponding monoenes. In accordance, (*E,Z*)-1,5-cyclodecadiene (vide infra), (*E,E,E*)-1,5,9-cyclododecatriene (Table I, entry 8) and (*E,E*)-1,5-dimethyl-1,5-cyclooctadiene (Table II, entry 13) all reacted considerably faster than their monounsaturated analogues. This is also true for 1,4-cyclohexadienes, as shown by earlier studies (e.g. Scheme III).[9]

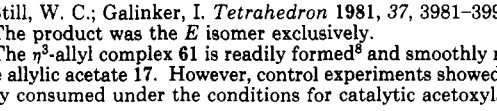
In addition to more efficient coordination, the introduction of additional double bonds may lead to dramatic changes in the mechanism. This is illustrated by the acetoxylation of (*E,Z*)-1,5-cyclodecadiene, which gives **33** as the major product (Scheme IV).[10] The mechanism for this rather unexpected transformation is probably Cope rearrangement to divinylcyclohexane,[11] followed by 1,2-acetoxypalladation, cyclization, and $\beta$-elimination of palladium hydride.[12]

The striking difference between the reactions of (*Z,Z*)-1,5-dimethyl-1,5-cyclooctadiene and (*E,Z*)-1,5-cyclodecadiene could be due partly to the difference in configuration of the double bonds. Comparison of the results from oxidation of (*E,E,E*)-cyclododecatriene and its *E,E,Z* isomer also suggests a difference: the *E,E,E* isomer gave one single product **7**, while the *E,E,Z* isomer gave a mixture of at least three products, none of which is **7**.[13]

The influence of substituents on the reactions of cycloalkenes was also studied. The reaction rates of alkyl-substituted cycloalkenes were comparable to those of the parent compounds, and the total yields were generally good. One exception is 1-methylcyclopentene, which gave only 25% optimized yield of a mixture of the four monoacetates **12–15** (Table II, entry 1). This result illustrates the major problem with the reactions of the substituted cycloalkenes, the formation of several isomeric products.

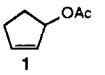
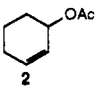
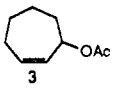
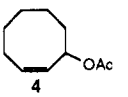
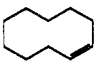
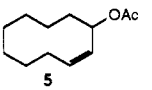
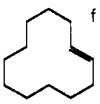
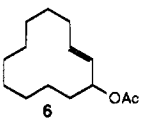
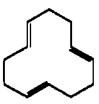
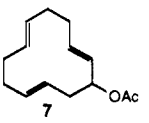
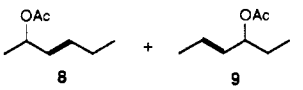
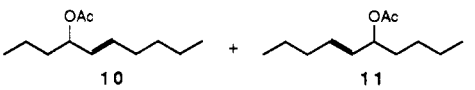
1-Methylcyclohexene gave a far better yield of acetates, and the selectivity is also better since two major products, **18** and **19**, are formed, accompanied by trace amounts of two other unidentified products (Table II, entry 4).[14]

(5) Still, W. C.; Galinker, I. *Tetrahedron* **1981**, *37*, 3981–3996.
(6) The product was the *E* isomer exclusively.
(7) The $\eta^3$-allyl complex **61** is readily formed[8] and smoothly reacts to give the allylic acetate **17**. However, control experiments showed that **17** is slowly consumed under the conditions for catalytic acetoxylation.




(8) Nakasuji, K.; Yamaguchi, M.; Murata, I.; Tatsumi, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1257–1260.
(9) (a) Söderberg, B. C. Ph.D. Thesis, Royal Institute of Technology, Stockholm, Sweden, 1987. (b) Söderberg, B. C.; Åkermark, B.; Hall, S. S. *J. Org. Chem.* **1988**, *53*, 2929–2937.
(10) Major component (52%) in a mixture of at least six products.
(11) Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579–586.
(12) (a) Heumann, A.; Reglier, M.; Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 866–867. (b) Antonsson, T.; Heumann, A.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1986**, 518–520.
(13) Hansson, S., unpublished results.
(14) 2-Methylidenecyclohexanol can be detected in the product from hydrolysis of the crude acetate mixture, which indicates that the corresponding acetate is one of the primary products.

**Table I. Oxidation of Unsubstituted Cycloalkenes and Linear Alkenes with $Pd(OAc)_2$/Benzoquinone/$MnO_2$ in Acetic Acid[a]**

| entry | substrate | temp, °C | time, h | conversion, %[b] | products | isolated yield, % |
|---|---|---|---|---|---|---|
| 1 |  | 50 | 16 | 95[c] |  **1** | 66 |
| 2 |  | 60 | 50 | 95 |  **2** | 77[d] |
| 3 |  | 25 | 16 | – | **2** | 36[e] |
| | | | 75 | – | | 82[e] |
| 4 |  | 60 | 28 | 98 |  **3** | 73 |
| 5 |  | 60 | 90 | 60 |  **4** | 35 |
| 6 |  | 60 | 300 | 93 |  **5** | 78 |
| 7 |  f | 60 | 43 | 77 |  **6** | 72 |
| 8 |  | 40 | 72 | 85 |  **7** | 60 |
| 9 |  | 60 | 72 | – |  **8** + **9** | >80[e,g] |
| 10 |  | 60 | 68 | 95 |  **10** + **11** | 74[g] |

[a] 5% $Pd(OAc)_2$, 20% benzoquinone, 110–200% $MnO_2$ in acetic acid (0.4 M in alkene). [b] For the substrates in this table, conversion is defined as allylic acetate/(allylic acetate + substrate). [c] Determined by NMR. [d] 0.5% $Pd(OAc)_2$, 10% benzoquinone. [e] GLC yield. [f] The substrate was a mixture of approximately 60% *E* isomer and 30% *Z* isomer, the remaining 10% being mainly cyclododecane. [g] A 1:1 mixture of regioisomers.

A phenyl substituent, such as in 1-phenylcyclohexene, has no major influence on the product pattern, which is similar to that from 1-methylcyclohexene, but rate and yield go down (Table II, entry 7). An alkoxycarbonyl substituent seems to have a similar influence, as indicated by a comparison between 4-methylcyclohexene and methyl 3-cyclohexenecarboxylate (Table II, entries 6 and 8). 3-Cyclohexenecarbonitrile and 3-cyclohexenyl methyl ketone appear to be totally unreactive, suggesting that a nitrile or acyl substituent inhibits the acetoxylation, perhaps by competing for coordination sites on palladium (Table II, entries 9 and 10). The position of the substituent does not appear to have any major influence on the rates and yields, since 3- and 4-methylcyclohexene both give high yields of a mixture of three major regioisomeric acetates, **19–21**, from 3-methylcyclohexene and **20–22** from 4-methylcyclohexene (Table II, entries 5 and 6). The compound **21** is a 1:1 mixture of trans and cis isomers, indicating a complete lack of face selectivity in the acetoxylation. We were not able to determine the trans:cis ratio for **20**. Since **20** and **21** are probably interconvertible under the reaction conditions,[11,15] **20** is also likely to be a 1:1 trans:cis mixture. In contrast, the trans:cis ratio for **22** is 52:6.

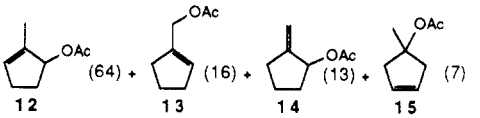
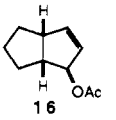
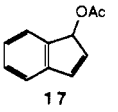
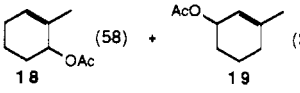
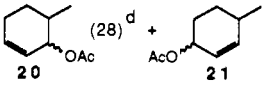
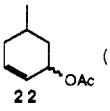
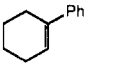
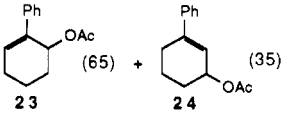
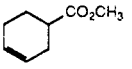
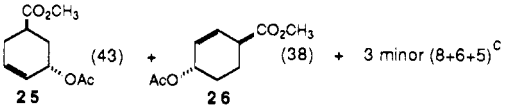
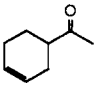
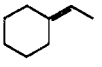
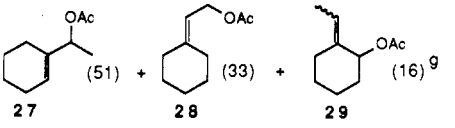
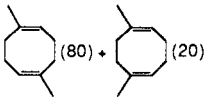
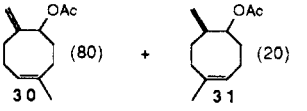
If the double bond is exocyclic, this can have a major influence on the catalytic acetoxylation, and methylenecyclohexane gave a complex mixture of products (Table II, entry 11). In contrast, ethylidenecyclohexane reacted to give three products **27–29** (Table II, entry 12). In order to understand these puzzling differences, and also be able to control the product distribution from the substituted cycloalkenes, it is necessary to understand more about the mechanism of acetoxylation.

## Mechanism

There are two reasonable pathways for the palladium-catalyzed allylic acetoxylation of alkenes: (i) 1,2-acetoxypalladation, followed by $\beta$-elimination of palladium hydride, and (ii) initial transformation of the alkene into a $\eta^3$-allyl complex, followed by nucleophilic attack of

(15) Henry, P. M. *Acc. Chem. Res.* **1973**, *6*, 16–24.

**Table II. Oxidation of Substituted Alkenes with $Pd(OAc)_2$/Benzoquinone/$MnO_2$ in Acetic Acid[a]**

| entry | substrate | temp, °C | time, h | conversion, % | products | isolated yield, % |
|---|---|---|---|---|---|---|
| 1 |  | 40 | 48 | 95 |  12 (64) + 13 (16) + 14 (13) + 15 (7) | 25 |
| 2 |  | 50 | 30 | 98 |  16 | 76 |
| 3 |  | 60 | 72 | 20 |  17 | <10[b] |
| 4 |  | 50 | 24 | 100 |  18 (58) + 19 (38) + 2 minor (2+2)[c] | 77 |
| 5 |  | 50 | 24 | 100 | 19 (48) +  20 (28)[d] + 21 (24)[e] | 73 |
| 6 |  | 50 | 24 | 100 |  22 (58)[f] + 20 (14)[d] + 21 (28)[e] | 85 |
| 7 |  | 50 | 72 | 70 |  23 (65) + 24 (35) | 53 |
| 8 |  | 50 | 72 | 60 |  25 (43) + 26 (38) + 3 minor (8+6+5)[c] | 42 |
| 9 |  | 60 | 24 | – | no reaction | – |
| 10 |  | 60 | 27 | – | no reaction | – |
| 11 |  | 60 | 24 | 64 | complex mixture | not det. |
| 12 |  | 50 | 42 | 100 |  27 (51) + 28 (33) + 29 (16)[g] | 54 |
| 13 |  (80) + (20) | 40 | 22 | 98 |  30 (80) + 31 (20) | 55 |

[a] 5% $Pd(OAc)_2$, 20% benzoquinone, 110–200% $MnO_2$ in acetic acid (0.4 M in alkene). [b] GLC yield. [c] Not identified. [d] Trans:cis ratio not determined. [e] Trans:cis ratio 1:1. [f] Trans:cis ratio 52:6. [g] Only one isomer, presumably *E*, observed.

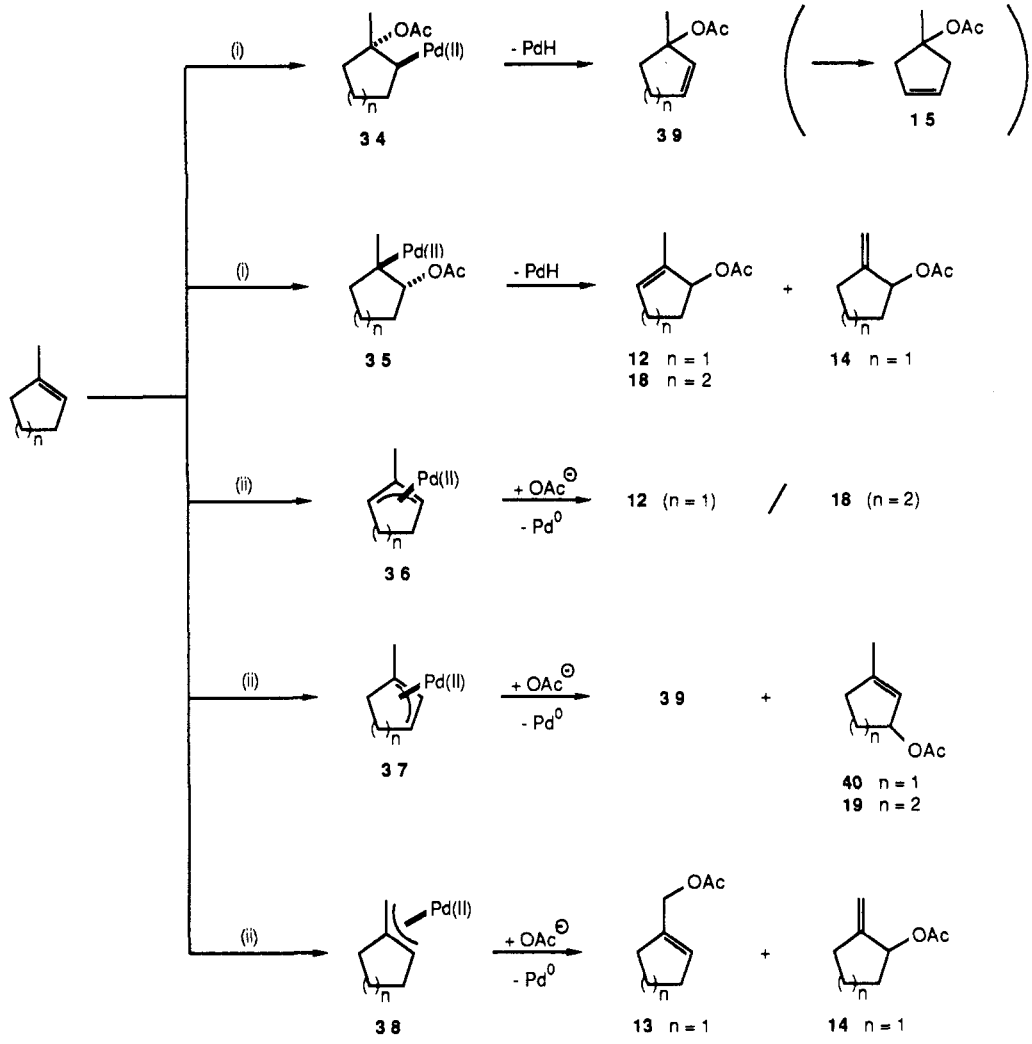
acetate. This is illustrated in Scheme V for 1-methylcycloalkenes.

For simple alkenes, an early study of the stoichiometric acetoxylation of 1- and 2-butene by palladium acetate shows that a $\eta^3$-allyl mechanism (ii) is improbable. The two alkenes, which must give the same $\eta^3$-allyl complex, give different products, 1-butene an 80:9:9 mixture of the vinyl acetates **41** and **42** and the allyl acetate **43**, and 2-butene essentially pure allyl acetate **44** (Scheme VI).[16]

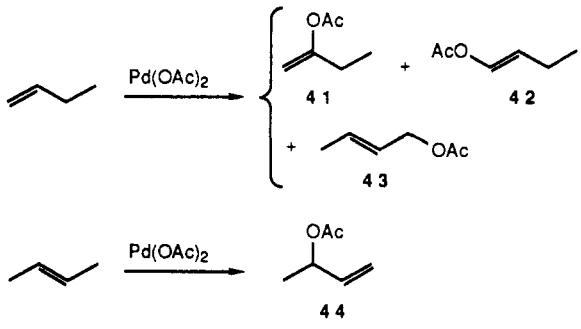
For the catalytic reaction, our results from oxidation of 3-hexene show that it is not possible to distinguish between the two mechanisms (i) and (ii). The reaction gave a 1:1 mixture of the allylic acetates **8** and **9** as required by the

(16) Kitching, W.; Rappoport, Z.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1966**, *88*, 2054–2055.

**Scheme V**




**Scheme VI**




$\eta^3$-allyl mechanism (ii) (Table I, entry 9). However, separate experiments showed that the acetate **9**, which should be formed as the only product in the alternative 1,2-acetoxypalladation (i), rapidly generated the observed 1:1 mixture of **8** and **9** under the reaction conditions (Scheme VII).

Mechanistic conclusions from the acetoxylation of the cycloalkenes meet with the same problem, although it has been found in experiments with specifically deuterated cyclohexene that the rearrangement of the allylic acetate is slower than its formation under certain conditions.[17] In this case, a $\eta^3$-allyl mechanism was suggested. Selective destruction of some of the primary products and further oxidation to diacetates can also influence the final product composition.[18] Some early experiments on methylenecycloalkanes also suggest that the mechanism depends on the substrate in a rather subtle way. It was found that methylenecyclohexane gave dimers via 1,2-acetoxypalladation[19] while methylenecycloheptane gave a mixture of the two monomeric acetates **45** and **46**, most probably via the $\eta^3$-allyl complex **38** ($n$ = 3) (Scheme VIII).[19]

In order to get further insight in the reaction mechanism, some of the substituted cycloalkenes were converted into $\eta^3$-allyl complexes according to published procedures.[20a,b] The $\eta^3$-allyl complexes were then subjected to the acetoxylation conditions, and the product compositions were compared with those obtained by catalytic acetoxylation of the parent alkenes. In one case strong indications of one single mechanism was obtained. This is the reactions of bicyclo[3.3.0]octene, which gave the same product **16**

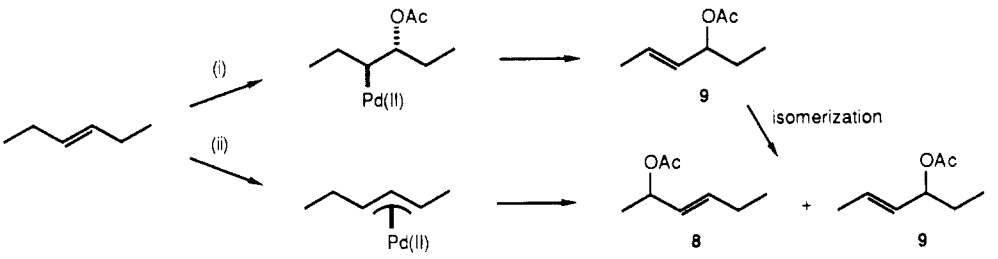
(17) (a) Wolfe, S.; Campbell, P. G. C. *J. Am. Chem. Soc.* **1971**, *93*, 1497–1499. Wolfe, S.; Campbell, P. G. C. *J. Am. Chem. Soc.* **1971**, *93*, 1499–1501. (b) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; Reidel: Dordrecht, 1980.

(18) Åkermark, B.; Hansson, S.; Rein, T.; Vågberg, J.; Heumann, A.; Bäckvall, J. E. *J. Organomet. Chem.* **1989**, *369*, 433.

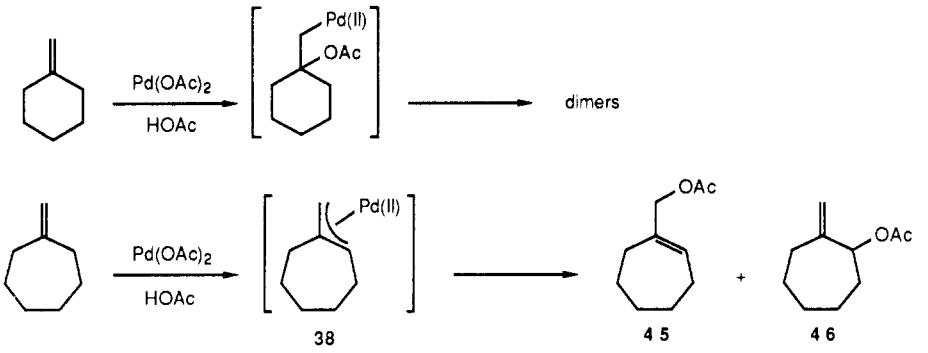
(19) Kikukawa, K.; Sakai, K.; Asada, K.; Matsuda, T. *J. Organomet. Chem.* **1974**, *77*, 131–145.

(20) (a) Trost, B. M.; Metzner, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3572–3577. (b) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407–3415. (c) Trost, B. M.; Strege, P. E. *Tetrahedron Lett.* **1974**, 2603–2606. For a review concerning $\eta^3$-allyl complexes, see: Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 6, pp 385–446.

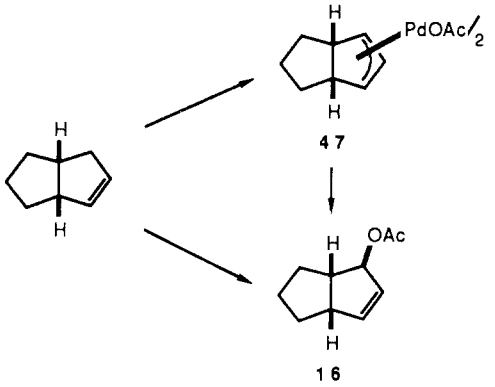
**Scheme VII**



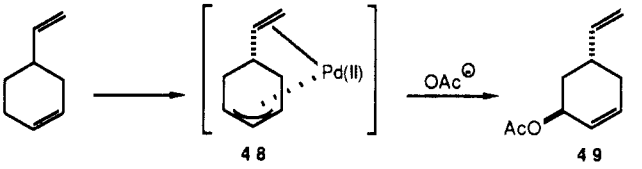

**Scheme VIII**




**Scheme IX**




**Scheme X**




both in the catalytic acetoxylation and in the acetoxylation of the preformed $\eta^3$-allyl complex **47** (Scheme IX).

The interpretation of the results from the reactions of the methylcycloalkenes is more difficult. Conversion of 1-methylcyclohexene into $\eta^3$-allyl complexes gave **36** ($n$ = 2) as the major product together with trace amounts of the isomeric complexes **37** ($n$ = 2) and **38** ($n$ = 2). Acetoxylation of this mixture gave essentially pure acetate **18**. This is also the major product from the catalytic reaction of the alkene (Table II, entry 4), but in addition this reaction gives substantial amounts of the isomeric acetate **19**. The formation of **19** is best explained by 1,2-acetoxypalladation (i) followed by $\beta$-elimination to give **39** as the initial product, and subsequent allylic rearrangement to **19** under the reaction conditions.[21] Thus, concurrent operation of both mechanisms (i) and (ii) in Scheme V explains these results.

For 1-methylcyclopentene the situation is even more complicated. It has earlier been shown that conversion of this compound into the $\eta^3$-allyl complex yields exclusively the exocyclic complex **38** ($n$ = 1).[20c] However, the catalytic acetoxylation gave only small amounts of the products **13** and **14**, which are the ones expected from reaction via a $\eta^3$-allyl mechanism (ii). The product **39** ($n$ = 1) and its rearrangement product **40** ($n$ = 1), which are expected from 1,2-acetoxypalladation, are at most observed as transients during the reaction. On the other hand, the formation of small amounts of the homoallylic acetate **15** provides indirect evidence for the acetoxypalladation mechanism: **15** is most probably formed from **39** via hydride migration. The absence of **39** and **40** ($n$ = 1) in the product in combination with the low optimized yield suggests that some type of selective decomposition of the primary products takes place.[22] Also for 1-methylcyclopentene a combination of the two reaction pathways (i) and (ii) thus offers the best explanation for the observed results, even though the main isomer **12** is not expected as a primary product from either mechanism.

The results from the transformations of a series of 4-substituted cyclohexenes, finally, are informative but as yet not conclusive. One of us has earlier shown that 4-vinylcyclohexene yields the acetate **49** as the exclusive product upon palladium-catalyzed acetoxylation using copper(II) chloride as stoichiometric oxidant.[23] The reaction probably proceeds via the $\eta^3$-allyl complex **48** (Scheme X).

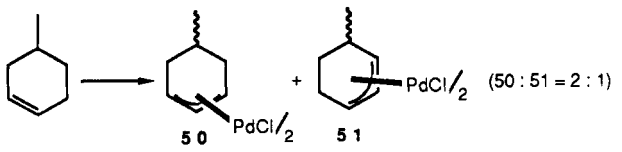
The acetoxylations of 4-methylcyclohexene and methyl 3-cyclohexenecarboxylate were far less specific, and mixtures of products were obtained (Table II, entries 6, 8). The results could be explained either by (a) 1,2-acetoxypalladation at both double bond termini, followed by allylic rearrangement, or (b) acetate addition at both termini of the two possible $\eta^3$-allyl complexes which are intermediates

(21) This is inferred from the properties of tertiary cyclohexenyl acetate **39** ($n$ = 2), which rearranged to **19** merely on attempted chromatography on silica.

(22) Under more acidic conditions, such selective decomposition is observed for the methylcyclohexenyl acetates.[18]

(23) Heumann, A.; Reglier, M.; Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1982**, 366–367; *Angew. Chem., Suppl.* **1982**, 922–927.

**Scheme XI**




in the alternative mechanism. Examination of models suggests that 1,2-acetoxypalladation should give approximately equal amounts of cis and trans product acetates from both 4-methylcyclohexene and methyl 3-cyclohexenecarboxylate. In contrast, both of the major products (**25** and **26**) from methyl 3-cyclohexenecarboxylate are trans isomers, presumably formed via a $\eta^3$-allyl mechanism. Preliminary experiments have shown that conversion of 4-methylcyclohexene to $\eta^3$-allyl complexes gives a ca. 2:1 mixture of the two complexes **50** and **51** (Scheme XI).[24] This corresponds moderately well to the ratio of ca. 1.3:1 between **22** and the sum of **21** and **20**, which is observed in the catalytic rection.

The relatively high stereoselectivity (52:6) in the formation of **22**, as contrasted to the low stereoselectivity in the formation of **21**, makes it tempting to suggest that **22** is derived mainly from acetate attack via palladium[25] on the trans $\eta^3$-allyl complex **50** and the isomers **20** and **21** are formed at least in part from acetoxypalladation. Furthermore, the fact that **20** and **21** are formed in different proportions from 4-methylcyclohexene and 3-methylcyclohexene indicates that they cannot only be formed via the $\eta^3$-allyl mechanism. It therefore appears that also for the 4-substituted cyclohexenes both mechanism (i) and (ii) operate concurrently. Further studies of the regio- and stereochemistry of the $\eta^3$-allyl complexes formed from different substituted cycloalkenes will provide valuable information about the importance of each mechanism. One crucial problem, which should be soluble by NMR studies, is the stereochemistry of the complexes **50** and **51**. Work along these lines is in progress.

## Conclusions

The palladium-catalyzed allylic acetoxylation described in this article is useful for unsubstituted cycloalkenes and a few special substrates, such as 1,5-dimethyl-1,5-cyclooctadiene, (*E,E,E*)-cyclododecatriene and *cis*-bicyclo[3.3.0]oct-2-ene. The mechanistic studies suggest that 1,2-acetoxypalladation and $\eta^3$-allyl formation [(i) and (ii), Scheme V] operate concurrently, the balance between the two pathways being delicate. There are indications from earlier work that the $\eta^3$-allyl route can be favored by use of more electrophilic catalysts than palladium acetate.[20a,26] As seen from the discussion above it should be possible to develop a much more selective oxidation process if proper conditions could be found to cleanly favor one mechanism over the other.

## Experimental Section

**General.** All solvents and reagents were purchased from commercial sources (Aldrich, BDH, Engelhardt, Fluka, Labassco, Merck, Riedel-de-Haen) and used as received, unless otherwise indicated. Dimethyl-1,5-cyclooctadiene was a generous gift from Dr. Erich Klein, Dragoco, Gerberding & Co., GmbH, 3450 Holzminden, FRG. Pentane (Labassco, 95%) was distilled before use. Methyl 3-cyclohexenecarboxylate[27] and di($\mu$-chloro)bis[(1,2,3-$\eta$)inden-1-yl]dipalladium[8] were prepared according to literature procedures. Bulb-to-bulb distillation refers to distillation with a Büchi GKR-50 Kugelrohr apparatus. Flash chromatography was performed as described by Still, Kahn, and Mitra.[28] Analytical TLC performed on Merck TLC aluminum sheets $F_{254}$ silica gel 60, precoated, using UV light and 5% phosphomolybdic acid in ethanol for visualization. NMR spectra were recorded on a Bruker WP 200 or a Bruker AM 400 instrument, with $CDCl_3$ as solvent. Chemical shifts are given in $\delta$ values relative to $(CH_3)_4Si$ (0.00 ppm) or $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm) as internal standards, for $^1H$ and $^{13}C$, respectively. $^1H$ NMR decoupling experiments were used to confirm the structural assignments of the products. The following abbreviations are used in descriptions of NMR multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, app = apparent, $J$ = coupling constant. GLC analysis was performed on a Varian 3700 instrument fitted with a BP-1 (methylsilicone, 25 m) or a OV-1 (vinylsilicone, 10 m) capillary column, or a Pye Unicam GCD instrument (5% SE-30 on Chromosorb W as stationary phase). $C_8$–$C_{16}$ *n*-alkanes were used as internal standards for GLC analyses. Analytical and preparative HPLC was performed on a Waters HPLC equipped with a M-45 pump, a R 401 differential refractometer, and a $\mu$-Porasil P/N 27477 analytical column. Elementary analyses were performed by Analytische Laboratorien, Engelskirchen, West Germany, and by the Service de Microanalyse de la Faculté de St.-Jérome, Marseille, France.

**Oxidations of Olefins, Optimized Conditions (General Procedure A).** A slurry of $Pd(OAc)_2$ (1.122 g, 5 mmol), benzoquinone (2.162 g, 20 mmol), and manganese dioxide (10.44 g, 120 mmol) in 250 mL of acetic acid, in a 500-mL round-bottomed flask fitted with a reflux condenser, was stirred at the reaction temperature for 30 min. The olefin (100 mmol) was added, and the mixture was stirred for the reported time. After cooling to room temperature, 250 mL of pentane–ether (1:1) was added, and the mixture was stirred for 30 min. The mixture was filtrated with suction through a Buchner funnel, containing a layer of Celite (5–10 mm). The Celite layer was 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 separation of the organic phase, the aqueous phase was extracted three times with 250 mL of pentane–ether (1:1). The combined organic phase was washed successively with 250 mL of water, 250 mL of 2 M NaOH, 100 mL of 2 M NaOH, and 250 mL of water and finally dried over 25 g of anhydrous $MgSO_4$. After evaporation of the solvent, the product was purified either by distillation or by flash chromatography.

Time and temperature are optimized for the reactions. In addition to time and temperature, optimized conversions are noted for every substrate, where optimized conversion is defined as allylic acetate/(allylic acetate + starting olefin). This conversion was calculated from GLC chromatograms using the area given by the integrator without using response factors (FID detector). All the reactions reported here are conveniently monitored by capillary GLC.

**Oxidation of Olefins, Nonoptimized Conditions (General Procedure B).** $Pd(OAc)_2$ (112 mg, 0.5 mmol, 5 mol %) and benzoquinone (216 mg, 2.0 mmol, 20 mol %) were dissolved in acetic acid (25 mL) and stirred at room temperature for 15 min. $MnO_2$ (1.74 g, 20 mmol, 200 mol %) and the olefin (10 mmol) were added, and the resulting mixture was heated to 50 °C for the indicated period of time. Extractive workup, as in the general procedure described above, and flash chromatography (mixtures of pentane and diethyl ether as eluent) or distillation gave the allylic acetates. The reactions were monitored by capillary GLC, and the conversion of the starting olefin determined by using an internal standard. The reactions were stopped when no starting olefin could be detected, or when the amount of monoacetates did not increase further.

**2-Cyclopenten-1-yl acetate (1):** optimized conditions (procedure A); reaction time 16 h, temperature 50 °C; optimized conversion more than 95% (NMR); yield 8.33 g (66%; bp 79–82 °C (60 mmHg)), contains about 5% homoallylic acetate according

(24) Heumann, A., unpublished results. The stereochemistry of complexes **50** and **51** has not been determined.
(25) Bäckvall, J.-E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892–6898.
(26) McMurry, J. E.; Kocovsky, P. *Tetrahedron Lett.* **1984**, *25*, 4187–4190.
(27) Inukai, T.; Kasai, M. *J. Org. Chem.* **1965**, *30*, 3567–3569.
(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

to capillary GLC; $^1$H NMR (200 MHz) $\delta$ 6.10 (m, 1 H), 5.83 (m, 1 H, H-2), 5.69 (m, 1 H), 2.03 (s, 3 H, OAc), 2.60–1.70 (m, 4 H); $^{13}$C NMR (100 MHz) $\delta$ 170.91, 137.41, 129.18, 80.35, 30.95, 29.65, 21.19. Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.71; H, 8.00.

**2-Cyclohexen-1-yl acetate (2)**: optimized conditions (procedure A); 0.5% $Pd(OAc)_2$ (0.112 g, 0.5 mmol), 10% benzoquinone (1.08 g, 10 mmol), 110% manganese dioxide (9.56 g, 110 mmol); reaction time 50 h, temperature 60 °C; optimized conversion 95% (GLC); yield 10.8 g (77%; bp 68 °C (15 mmHg)), contains about 1.5% homoallylic acetate according to capillary GLC. The $^1$H NMR[29] and $^{13}$C NMR[30] spectra of the product were in full accordance with those reported in the literature.

**2-Cyclohepten-1-yl acetate (3)**: optimized conditions (procedure A); reaction time 28 h, temperature 60 °C; optimized conversion 98% (GLC); yield 11.24 g (73%; bp 61–62 °C (5 mmHg)), contains less than 0.5% homoallylic acetate according to GLC; $^1$H NMR (200 MHz) $\delta$ 5.82 (m, 1 H), 5.65 (m, 1 H), 5.40 (m, 1 H), 2.05 (s, 3 H), 2.30–1.30 (m, 8 H); $^{13}$C NMR[30] (100 MHz) $\delta$ 170.24, 133.56, 131.38, 74.13, 32.70, 28.33, 26.48, 26.43, 21.20. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.18; H, 9.07.

**2-Cycloocten-1-yl acetate (4)**: optimized conditions (procedure A); 200% manganese dioxide (17.4 g, 200 mmol), reaction time 90 h, temperature 60 °C; optimized conversion 60% (GLC); yield 5.8 g (35%; bp 63–64 °C (3 mmHg)), contains about 5% homoallylic acetate according to GLC. 15% unreacted cyclooctene was recovered from the reaction by distillation; $^1$H NMR (400 MHz) $\delta$ 5.65 (m, 2 H), 5.45 (m, 1 H), 2.24 (m, 1 H), 2.10 (m, 1 H), 2.03 (s, 3 H), 1.89 (m, 1 H), 1.73–1.32 (m, 7 H); $^{13}$C NMR (100 MHz) $\delta$ 170.38, 130.64, 129.64, 72.28, 35.05, 28.73, 26.28, 25.77, 23.31, 21.33. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.47; H, 9.30.

**(*Z*)-2-Cyclodecen-1-yl acetate (5)**: optimized conditions (procedure A); 20-mmol scale, reaction time 300 h, temperature 60 °C; optimized conversion 93% (GLC); yield 2.88 g (78%; flash chromatography, eluene hexane–ether, 95:5), purity ca. 98% according to GLC; $^1$H NMR (200 MHz) $\delta$ 5.90 (dt, $J$ = 10.5, 5 Hz, 1 H, H-3), 5.53 (dt, $J$ = 10.5, 5.3 Hz, 1 H, H-1), 5.32 (app t, $J$ = 10.5 Hz, 1 H, H-2), 2.78–2.55 (m, 1 H, H-4), 2.12–1.95 (m, 1 H, H-4), 2.01 (s, 3 H, OAc), 1.90–1.20 (m, 12 H); $^{13}$C NMR (100 MHz) $\delta$ 170.29, 133.09, 128.78, 70.33, 33.40, 27.25, 25.23, 25.06, 24.16, 21.39, 20.78, 20.43. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.44; H, 10.22.

**(*E*)-2-Cyclododecen-1-yl acetate (6)**: optimized conditions (procedure A); 20-mmol scale, reaction time 43 h, temperature 60 °C; optimized conversion 77% (GLC); yield 3.24 g (72%; flash chromatography, eluent hexane–ether, 95:5); two unknown products were present in about 3% and 4% according to GLC; $^1$H NMR (200 MHz) $\delta$ 5.70 (ddd, $J$ = 14.9, 9.4, 5.1 Hz, 1 H, H-3), 5.38 (ddt, $J$ = 14.9, 7.6, 0.7 Hz, 1 H, H-2), 5.17 (d app t, $J$ = 8.8, 4.1 Hz, 1 H, H-1), 2.02 (s, 3 H, OAc), 2.3–1.2 (m, 18 H); $^{13}$C NMR (100 MHz) $\delta$ 170.14, 135.04, 129.11, 75.89, 31.97, 31.56, 25.74, 25.48, 24.78 (2 C), 24.44, 24.22, 22.21, 21.38. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.86; H, 10.57. According to capillary GLC and $^1$H NMR the starting material was a mixture of 65% (*E*)-cyclododecene, 28% (*Z*)-cyclododecene, and 7% cyclododecane. From the reaction, 20% of "starting material" was recovered, now as a mixture containing about 20% (*E*)-cyclododecene, 50% (*Z*)-cyclododecene, and 30% of cyclododecane.

**(*E,E,E*)-2,6,10-Cyclododecatrien-1-yl acetate (7)**: optimized conditions (procedure A); 20-mmol scale, 200% manganese dioxide (3.48 g, 40 mmol), reaction time 72 h, temperature 40 °C; optimized conversion 85% (GLC); yield 2.64 g (60%; flash chromatography, eluene hexane–ether, 95:5), purity >99% (GLC); $^1$H NMR (200 MHz) $\delta$ 5.40–4.95 (m, 7 H), 2.04 (s, 3 H), 2.47–1.85 (m, 10 H); $^{13}$C NMR (50 MHz) $\delta$ 170.12, 134.57, 134.16, 131.50, 130.89, 129.74, 126.11, 75.10, 37.95, 32.30, 32.18, 31.88, 31.81, 21.37. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.30; H, 9.19.

**(*E*)-3-Hexen-2-yl acetate (8) and (*E*)-4-hexen-3-yl acetate (9)**: optimized conditions (procedure A); 2-mmol scale, reaction time 72 h, temperature 60 °C; yield 85% (calculated from capillary GLC using *n*-decane as internal standard); product structures were verified by comparing their $^1$H NMR, $^{13}$C NMR, and retention time on GLC with authentic samples prepared by Grignard reactions of ethylmagnesium bromide with (*E*)-2-butenal, and methylmagnesium bromide with (*E*)-2-pentenal, respectively, followed by acetylation. **8**: $^1$H NMR (200 MHz) $\delta$ 5.75 (dt, $J$ = 14.7, 6.1 Hz, 1 H, H-4), 5.45 (ddt, $J$ = 15.1, 6.7, 1.5 Hz, 1 H, H-3), 5.32 (app quintet of d, $J$ = 6.5, 0.6 Hz, 1 H, H-2), 2.05 (m, 2 H, H-5), 2.04 (s, 3 H, OAc), 1.29 (d, $J$ = 6.3, Hz, 3 H, H-1), 0.99 (t, $J$ = 7.5 Hz, 3 H, H-6); $^{13}$C NMR (50 MHz) $\delta$ 169.36, 133.98, 128.06, 70.83, 25.06, 21.22, 20.32, 13.17. **9**: $^1$H NMR (200 MHz) $\delta$ 5.72 (ddq, $J$ = 15.3, 0.7, 6.4 Hz, 1 H, H-5), 5.40 (ddq, $J$ = 15.3, 7.3, 1.5 Hz, 1 H, H-4), 5.11 (app q, $J$ = 6.8 Hz, 1 H, H-3), 2.04 (s, 3 H, OAc), 1.69 (ddd, $J$ = 6.5, 1.5, 0.6 Hz, 3 H, H-6), 1.70–1.50 (m, 2 H, H-2), 0.88 (t, $J$ = 7.4 Hz, 3 H, H-1); $^{13}$C NMR (50 MHz) $\delta$ 169.30, 128.86, 128.26, 75.71, 27.44, 21.15, 17.56, 9.45.

**(*E*)-5-Decen-4-yl acetate (10) and (*E*)-6-decen-5-yl acetate (11)**: optimized conditions (procedure A); 20-mmol scale, 200% manganese dioxide (3.48 g, 40 mmol), reaction time 68 h, temperature 60 °C; optimized conversion 95% (GLC); yield 2.95 g (74%; flash chromatography, eluent hexane–ether, 95:5), of a 1:1 mixture of **10** and **11** (GLC). Ordinary $^1$H NMR analysis together with decoupling experiments led to the tentative structure assignments: $^1$H NMR (200 MHz; 1:1 mixture of **10** and **11**) $\delta$ 5.69 (dt, $J$ = 15, 6.6 Hz, 2 H, H-6(**10**), H-7(**11**)), 5.36 (dd, $J$ = 15, 7.3 Hz, 2 H, H-5(**10**), H-6(**11**)), 5.18 (app qd, $J$ = 7.3 Hz, 2 H, H-4(**10**), H-5(**11**)), 2.033 (s, 3 H, OAc), 2.031 (s, 3 H, OAc), 2.05–1.20 (m, 12 H), 0.95–0.83 (m, 12 H; 4 Me); $^{13}$C NMR (100 MHz) $\delta$ 170.27 (2 C), 134.24, 134.03, 128.51, 128.26, 74.97, 74.74, 36.59, 34.17 (2 C), 31.79, 31.05, 27.28, 22.35, 22.06, 22.02, 21.24 (2 C), 18.37, 13.85, 13.77, 13.71, 13.46. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.67; H, 11.16.

**Oxidation of 1-methylcyclopentene**: optimized conditions (procedure A); 20-mmol scale, 200% manganese dioxide (3.48 g, 40 mmol), reaction time 48 h, temperature 40 °C; optimized conversion 90% (GLC); yield 0.65 g (25%; flash chromatography, hexane–ether 95:5) of a mixture containing four monoacetates in a ratio of **12**:**13**:**14**:**15** = 64:16:13:7, according to capillary GLC. Further separation of the mixture by flash chromatography (elution with a stepwise gradient of 1–20% ether in pentane; as stationary phases were used both pure silica gel and silica gel with adsorbed $AgNO_3$, 10% by weight) gave product **12** and **15** pure, **13** in a mixture with 40% **12** and **14** in a mixture with 40% **15**. Ordinary $^1$H NMR analysis together with extensive decoupling experiments led to the following structure determinations. 2-Methyl-2-cyclopenten-1-yl acetate (**12**): $^1$H NMR (200 MHz) $\delta$ 5.70–5.55 (m, 2 H), 2.51–2.15 (m, 3 H), 2.06 (s, 3 H, OAc), 1.85–1.72 (m, 1 H, H-5), 1.73–1.70 (m, 3 H, Me). $^{13}$C NMR of the corresponding alcohol, prepared via hydrolysis (MeOH, NaOH, 55 °C, 1 h) of the acetate, was in full accordance with a spectrum reported previously.[31] (1-Cyclopenten-1-yl)methyl acetate (**13**) and 2-methylenecyclopenten-1-yl acetate (**14**): $^1$H NMR data were in full accordance with those reported in the literature.[19] 1-Methyl-3-cyclopenten-1-yl acetate (**15**): $^1$H NMR $\delta$ 5.63 (br s, 2 H, H-3, H-4), 2.80 (br d, $J$ = 15.2 Hz, 2 H, H-2 (1 proton), H-5 (1 proton)), 2.42 (br d, $J$ = 15.9 Hz, 2 H, H-2 (1 proton), H-5 (1 proton)), 1.99 (s, 3 H, OAc), 1.57 (s, 3 H, Me).

***exo*-Bicyclo[3.3.0]oct-3-en-2-yl acetate (16)**: optimized conditions (procedure A); reaction time 30 h, temperature 50 °C; optimized conversion 98% (GLC); yield 12.64 g (76%; bp 60–62 °C) (3 mmHg)), purity ca. 97%; $^1$H NMR (200 MHz) $\delta$ 5.90 (ddd, $J$ = 5.6, 2.2, 0.9 Hz, 1 H, H-4), 5.68 (d app t, $J$ = 5.6, 2.2 Hz, 1 H, H-3), 5.34 (app q, $J$ = 2.2 Hz, 1 H, H-2), 3.33 (m, 1 H, H-5), 2.50 (m, 1 H, H-1), 2.03 (s, 3 H, OAc), 1.82–1.25 (m, 6 H); $^{13}$C NMR (100 MHz) $\delta$ 170.68, 141.80, 128.08, 87.58, 49.22, 47.88, 31.96, 30.46, 24.44, 21.04. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.32; H, 8.50. $^{13}$C NMR of the corresponding alcohol, prepared via hydrolysis of the acetate, was in full accordance with data reported previously.[32]

**Oxidation of indene**: nonoptimized conditions (procedure B); 2-mmol scale, 200% manganese dioxide (0.348 g, 4.0 mmol),

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reaction time 72 h, temperature 60 °C; conversion 20% (GLC); Yield ca. 10% according to GLC; flash chromatography (hexane–ether, 95:5) delivered a sample of pure **17**; $^1$H NMR (400 MHz) δ 7.45–7.17 (m, 4 H), 6.82 (ddd, $J$ = 5.8, 1.5, 0.7 Hz, 1 H, H-3), 6.37 (dd, $J$ = 5.8, 2.1 Hz, 1 H, H-2), 6.23 (br m, 1 H, H-1), 2.15 (s, OAc); $^{13}$C NMR (100 MHz) δ 171.38, 142.91, 141.98, 134.79, 133.35, 128.93, 126.27, 124.27, 121.59, 77.41, 21.08.

**Oxidation of 1-Methylcyclohexene**: nonoptimized conditions (procedure B); 100-mmol scale, 24 h, 100% conversion; 11.95 g (77%) of a mixture of allylic acetates was obtained after distillation (bp 81–82 °C (10 mmHg)). The main components were separated by preparative HPLC and identified as 2-methyl-2-cyclohexen-1-yl acetate (**18**) and 3-methyl-2-cyclohexen-1-yl acetate (**19**) by comparison of spectral data with those reported.[33] Capillary GLC of the isomeric mixture indicated that small amounts (≤4%) of two other isomers were also formed. **18**: $^1$H NMR (200 MHz), δ 5.66 (m, 1 H, H-3), 5.19 (br t, $J$ = 4 Hz, 1 H, H-1), 2.12–1.88 (m, 2 H), 2.05 (s, 3 H, OAc), 1.78–1.74 (m, 2 H), 1.63 (d, $J$ = 1.9 Hz, 3 H, C(2)-Me), 1.64–1.50 (m, 2 H); $^{13}$C NMR (100 MHz) δ 170.99, 131.64, 127.84, 70.66, 28.85, 25.09, 21.25, 20.40, 18.28. **19**: $^1$H NMR (200 MHz) δ 5.44 (m, 1 H, H-2), 5.22 (m, 1 H, H-1), 2.02 (s, 3 H, OAc), 2.02–1.83 (m, 2 H), 1.82–1.55 (m, 4 H), 1.69 (m, 3 H, C(2)-Me); $^{13}$C NMR (100 MHz) δ 170.80, 141.01, 120.01, 68.78, 29.87, 27.97, 23.65, 21.38, 18.99. Anal. (isomeric mixture) Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.03; H, 9.06.

Hydrolysis (2M NaOH, MeOH, 25 °C, overnight) of the mixture of allylic acetates gave the known corresponding allylic alcohols, whose spectral data agreed well with those reported.[31,33] According to NMR,[34] a small amount of the isomeric alcohol 2-methylidenecyclohexan-1-ol (**52**) was also present, which indicates that one of the minor acetate isomers is the corresponding acetate (**53**). 2-Methyl-2-cyclohexen-1-ol (**54**): $^1$H NMR (200 MHz) δ 5.55 (m, 1 H, H-3), 3.99 (m, 1 H, H-1), 2.10–1.90 (m, 2 H), 1.90–1.35 (m, 5 H), 1.77 (d, $J$ = 1.5 Hz, 3 H, C(2)-Me); $^{13}$C NMR (100 MHz) δ 135.26, 125.38, 68,35, 32.14, 25.36, 20.55, 18.11. 3-Methyl-2-cyclohexen-1-ol (**55**): $^1$H NMR (200 MHz) δ 5.49 (m, 1 H, H-2), 4.18 (m, 1 H, H-1), 2.07–1.45 (m, 7 H), 1.69 (m, 3 H, C(2)-Me); $^{13}$ NMR (100 MHz) δ 138.47, 124.27, 65.75, 31.58, 29.99, 23.53, 18.97. **52**: $^1$H NMR (200 MHz, in mixture with **54**) δ 4.89 (m, 1 H), 4.76 (m, 1 H).

**Oxidation of 3-methylcyclohexene**: nonoptimized conditions (procedure B); 10-mmol scale, 24 h, 100% conversion; flash chromatography gave 73% yield of a mixture of allylic acetates. According to $^1$H NMR, the main component was **19**. Anal. (isomeric mixture) Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.01; H, 9.12. The proportions of different acetate isomers were determined as described previously,[35] by hydrogenation ($H_2$, Pd/C (cat.), diethyl ether, 25 °C, overnight) of the mixture to the corresponding saturated acetates, and analysis by capillary GLC (authentic samples of the saturated acetates were prepared from the commercially available alcohols).

**Oxidation of 4-methylcyclohexene**: nonoptimized conditions (procedure B); 10-mmol scale, 24 h, 100% conversion. Flash chromatography gave 85% yield of a mixture of allylic acetates. According to $^1$H NMR, the main component was *trans*-5-methyl-2-cyclohexen-1-yl acetate (**22**): $^1$H NMR (200 MHz) assigned from spectrum of the isomeric mixture) δ 5.97 (br ddd, $J$ = 9.8, 5.2, 2.2 Hz, 1 H), 5.74 (m, 1 H), 5.22 (m, 1 H, H-1), 2.2–1.5 (m, 4 H), 2.01 (s, 3 H, OAc), 1.39 (ddd, $J$ = 14.2, 12.2, 4.3 Hz, 1 H, pseudo-axial H-6), 0.95 (d, $J$ = 6.5 Hz, 3 H, C(5)-Me). Anal. (isomeric mixture) Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.97; H, 9.01. The isomer distribution was determined in the same way as for the product from 3-methylcyclohexene (hydrogenation, capillary GLC analysis).

**Oxidation of 1-phenylcyclohexene**: nonoptimized conditions (procedure B); 2-mmol scale, 72 h, 70% conversion. After flash chromatography, 229 mg (53%) of a mixture of two acetates was obtained, together with 39 mg (12%) of unreacted starting olefin. The acetate isomers were separated by preparative HPLC, and the structure were assigned as 2-phenyl-2-cyclohexen-1-yl acetate (**23**) and 3-phenyl-2-cyclohexen-1-yl acetate (**24**) on the basis of spectral data. **23**: $^1$H NMR (400 MHz) δ 7.34–7.20 (m, 5 H), 6.33 (dd, $J$ = 4.8, 3.2 Hz, 1 H, H-3), 5.94 (br t, $J$ = 4.0 Hz, 1 H, H-1), 2.32 (m, 1 H), 2.20 (m, 1 H), 2.01–1.66 (m, 4 H), 1.94 (s, 3 H, OAc); $^{13}$C NMR (100 MHz) δ 170.71, 139.50, 135.47, 131.00, 128.31, 127.03, 125.49, 67.40, 28.96, 25.83, 21.24, 17.51. **24**: $^1$H NMR (400 MHz) δ 7.42–7.24 (m, 5 H), 6.08 (dt, $J$ = 3.9, 1.8 Hz, 1 H, H-2), 5.46 (m, 1 H, H-1), 2.52 (m, 1 H), 2.36 (m, 1 H), 2.07 (s, 3 H, OAc), 1.96–1.75 (m, 4 H); $^{13}$C NMR (100 MHz) δ 170.83, 142.14, 141.08, 128.28, 127.61, 125.43, 122.30, 68.94, 27.98, 27.34, 21.40, 19.40. Anal. (isomeric mixture) Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.53; H, 7.49. Hydrolysis (2 M NaOH, MeOH, 25 °C, 1 h) of the acetates afforded the known[34,36] allylic alcohols. 2-Phenyl-2-cyclohexen-1-ol (**56**): $^1$H NMR (400 MHz) δ 7.47–7.22 (m, 5 H), 6.15 (dd, $J$ = 4.7, 3.4 Hz, 1 H, H-3), 4.69 (m, 1 H, H-1), 2.25 (m, 1 H), 2.15 (m, 1 H), 1.98–1.63 (m, 5 H); $^{13}$C NMR (100 MHz) δ 140.15, 139.05, 128.61, 128.46, 127.03, 125.95, 65.38, 31.51, 26.00, 17.28. 3-Phenyl-2-cyclohexen-1-ol (**57**): $^1$H NMR (400 MHz) δ 7.41–7.23 (m, 5 H), 6.12 (dt, $J$ = 3.6, 1.8 Hz, 1 H, H-2), 4.38 (m, 1 H, H-1), 2.48 (m, 1 H), 2.36 (m, 1 H), 1.98–1.85 (m, 2 H), 1.79–1.60 (m, 3 H); $^{13}$C NMR (100 MHz) δ 141.43, 140.11, 128.27, 127.40, 126.54, 125.36, 66.30, 31.66, 27.48, 19.42.

**Oxidation of methyl 3-cyclohexenecarboxylate**: nonoptimized conditions (procedure B); 2-mmol scale, 72 h, 60% conversion. Flash chromatography afforded 165 mg (42%) of a mixture of allylic acetates, together with 32 mg (11%) of unreacted starting material. The two major product isomers were partially separated by preparative HPLC, and assignments based on their spectral data. *trans*-5-Carbomethoxy-2-cyclohexen-1-yl acetate[37] (**25**): $^1$H NMR (400 MHz, in mixture with **26**) δ 6.00 (m, 1 H), 5.81 (m, 1 H), 5.27 (m, 1 H, H-1), 3.70 (s, 3 H, COOMe), 2.78 (m, 1 H, H-5), 2.39 (dtt, $J$ = 18.2, 5.3, 1.4 Hz, 1 H), 2.25–2.14 (m, 2 H), 2.04 (s, 3 H, OAc), 1.83 (ddd, $J$ = 14.3, 12.7, 4.3 Hz, 1 H, pseudoaxial H-6). *trans*-4-Carbomethoxy-2-cyclohexen-1-yl acetate[38] (**26**): $^1$H NMR (400 MHz) δ 6.00 (br ddd, $J$ = 10.1, 3.1, 1.3 Hz, 1 H), 5.82 (br dt, $J$ = 10.1, 2.9 Hz, 1 H), 5.28 (m, 1 H, H-1), 3.71 (s, 3 H, COOMe), 3.17 (m, 1 H, H-4), 2.15–2.02 (m, 2 H), 2.05 (s, 3 H, OAc), 1.89 (ddd, $J$ = 10.5, 7.6, 3.7 Hz, 1 H), 1.67 (ddd, $J$ = 10.0, 7.2, 2.9 Hz, 1 H); $^{13}$C NMR (100 MHz) δ 173.58, 170.61, 128.93, 128.31, 67.81, 52.04, 40.78, 31.29, 26.81, 22.31, 21.27. Anal. (isomeric mixture) Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.43; H, 7.18.

**Oxidation of ethylidenecyclohexane**: nonoptimized conditions (procedure B); 10-mmol scale, 42 h, 100% conversion. After flash chromatography, 910 mg (54%) of a mixture of allylic acetates was obtained. The main product isomers were partially separated by preparative HPLC and characterized by their spectral data. 1-(Cyclohex-1-en-1-yl)eth-1-yl acetate (**27**): $^1$H NMR (400 MHz, in mixture with **28**) δ 5.68 (m, 1 H, C*H*=C), 5.21 (br q, $J$ = 6.6 Hz, 1 H, H-1), 2.02 (s, 3 H, OAc), 2.01–1.87 (m, 4 H), 1.76–1.38 (m, 4 H), 1.27 (d, $J$ = 6.6 Hz, 3 H, C(1)-Me); $^{13}$C NMR (100 MHz, in mixture with **28**) δ 170.38, 137.06, 123.57, 74.10, 24.18, 24.08, 22.42, 22.27, 21.31, 18.75. 2-Ethylidenecyclohex-1-yl acetate (**28**): $^1$H NMR (400 MHz, peaks possible to assign from spectrum of mixture with **27**) δ 5.40 (q app q, $J$ = 6.8, 1.0 Hz, 1 H, C*H*=C), 5.17 (m, 1 H, H-1), 2.04 (s, 3 H, OAc). 2-Cyclohexylideneeth-1-yl acetate (**29**): $^1$H NMR (400 MHz) δ 5.26 (t app quintets, $J$ = 7.3, 1.2 Hz, 1 H, H-2), 4.55 (d, $J$ = 7.3 Hz, 2 H, H-1), 2.19–2.15 (m, 2 H), 2.12–2.08 (m, 2 H), 2.02 (s, 3 H, OAc), 1.58–1.48 (m, 6 H); $^{13}$C NMR (100 MHz) δ 171.00, 146.78, 115.10, 60.56, 36.92, 28.93, 28.24, 27.64, 26.53, 20.99. Anal. (isomeric mixture) Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.29; H, 9.56. To confirm the structural assignments, the products were hydrolyzed (2 M NaOH, MeOH, room temperature, overnight) to the corresponding allylic alcohols. 1-(Cyclohex-1-en-1-yl)ethan-1-ol (**58**): $^1$H NMR[39] (200 MHz) δ 5.67 (m, 1 H, C*H*=C), 4.17 (br q, $J$ = 6.4 Hz, 1 H, H-1), 2.09–1.95 (m, 4 H),

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1.73–1.49 (m, 4 H), 1.48 (s, 1 H, O*H*), 1.26 (d, $J$ = 6.4 Hz, 3 H, C(1)-Me); $^{13}$C NMR (100 MHz) δ 141.24, 121.51, 72.15, 24.88, 23.66, 22.63, 22.58, 21.49. 2-Ethylidenecyclohexan-1-ol (**59**): $^1$H NMR (200 MHz, peaks possible to assign from spectrum of mixture with **58**) δ 5.43 (q app q, $J$ = 6.8, 1.2 Hz, 1 H, C*H*=C), 4.1 (m, 1 H, C*H*OH). 2-Cyclohexylideneethan-1-ol (**60**): $^1$H NMR[40] (200 MHz) δ 5.37 (t app quintets, $J$ = 7.1, 1.2 Hz, 1 H, H-2), 4.14 (d, $J$ = 7.1 Hz, 2 H, H-1), 2.26–2.06 (m, 4 H), 1.66–1.46 (m, 6 H), 1.3 (br s, 1 H, O*H*); $^{13}$C NMR (100 MHz) δ 144.44, 120.28, 58.51, 37.02, 28.82, 28.38, 27.85, 26.67.

**Oxidation of dimethyl-1,5-cyclooctadienes**: optimized conditions (procedure A); the starting material consisted of a mixture of 80% 1,5-dimethyl-1,5-cyclooctadiene and 20% 2,5-dimethyl-1,5-cyclooctadiene, 17-mmol scale, 200% manganese dioxide (2.96 g, 34 mmol), reaction time 22 h, temperature 40 °C; optimized conversion 98% (GLC); yield 1.81 g (55%; flash chromatography, eluent hexane–ether, 95:5) of a mixture consisting of 80% 4-methyl-8-methylene-4-cycloocten-1-yl acetate (**30**) and 20% 5-methyl-8-methylene-4-cycloocten-1-yl acetate (**31**). **30**: $^1$H NMR (400 MHz; in mixture with **31**) δ 5.38 (tq, $J$ = 8, 1.5 Hz, 1 H, H-5), 5.01 (d, $J$ = 1.5 Hz, 1 H), 4.91 (dd, $J$ = 10.5, 4.5 Hz, 1 H, H-1), 4.87 (br s, 1 H), 2.34–1.57 (m, 8 H), 1.99 (s, 3 H, OAc), 1.69 (br s, 3 H, C(4)-Me); $^{13}$C NMR (100 MHz) δ 170.2, 151.7, 136.5, 124.0, 112.1, 75.5, 37.4, 32.2, 27.0, 26.8, 23.1, 21.2. **31**: $^1$H NMR (400 MHz; in mixture with **30**) δ 5.34 (tq, $J$ = 8, 1.5 Hz, 1 H, H-4), 5.00 (d, $J$ = 1.5 Hz, 1 H), 4.94 (dd, $J$ = 10.5, 4.5 Hz, 1 H, H-1), 4.85 (br s, 1 H), 2.34–1.57 (m, 8 H), 2.00 (s, 3 H, OAc), 1.67 (br s, 3 H, C(5)-Me); $^{13}$C NMR (100 MHz) δ 170.1, 151.1, 137.2, 123.2, 112.0, 75.8, 35.2, 35.0, 30.6, 23.5 (two $CH_2$ carbons are hidden by signals from **30**). Anal. (isomeric mixture) Calcd for $C_{12}H_{18}O_2$: C, 74.15; H, 9.34. Found: C, 74.17; H, 9.37.

**Preparation of $\eta^3$-Allylpalladium Complexes. Di(μ-chloro)bis[(1,2,3-η)-2-methyl-2-cyclohexen-1-yl]dipalladium (36, $n$ = 2)** was prepared according to a published procedure.[20c] The complex was acetoxylated according to the general procedure for reactions with preformed $\eta^3$-allylpalladium complexes (vide infra) to give acetate **18** as the only isolated product.

**Di(μ-chloro)bis[(1,2,3-η)-1-methyl-2-cyclohexen-1-yl]dipalladium (37, $n$ = 2)** was prepared according to a published procedure[41] from 3-methyl-2-cyclohexen-1-ol (2.5-mmol scale). The product was purified by flash chromatography (eluent hexane–ether, 7:3): yield 0.41 g (70%); $^1$H NMR (200 MHz) δ 5.31 (br d, $J$ = 6.5 Hz, 1 H, H-2), 4.93 (ddd, $J$ = 6.5, 4.1, 2.1 Hz, 1 H, H-3), 2.20–1.50 (m, 4 H), 1.44 (s, 3 H, Me), 1.25–1.05 (m, 2 H); $^{13}$C NMR (50 MHz) δ 101.4, 95.3, 74.6, 35.0, 29.1, 27.8, 25.3.

The corresponding di(μ-acetato) complex **37′** was prepared from the chloride complex **37** by stirring with equimolar amounts of AgOAc (0.2 mmol) in 5 mL of acetone (p.a.) for 2 h at 0 °C in the dark.[42] The solubility of AgOAc in acetone is low, but the exchange is complete within 2 h. The mixture was filtered, and solvent was evaporated in vacuo at 0 °C: $^1$H NMR (200 MHz) δ 5.19 (br d, $J$ = 6 Hz, 1 H, H-2), 4.77–4.63 (br m, 1 H, H-3), 2.20–1.57 (m, 5 H), 2.00 (s, 3 H, OAc), 1.30 (s, 3 H, Me), 1.15–0.95 (m, 1 H). The complex was prepared just prior to use, and no further purification was attempted because of its lability at temperatures above 0 °C.

**Di(μ-chloro)bis[(2,3,4-η)-*cis*-bicyclo[3.3.0]oct-3-en-2-yl]dipalladium (47)** was prepared according to a published method[20a] from *cis*-bicyclo[3.3.0]oct-2-ene: $^1$H NMR (200 MHz) δ 5.62 (t, $J$ = 3.2 Hz, 1 H, H-3), 5.08 (d, $J$ = 3.2 Hz, 2 H, H-2, H-4), 2.62 (br s, 2 H, H-1, H-5), 1.50–1.25 (m, 6 H); $^{13}$C NMR (50 MHz) δ 100.85, 86.35 (2 C), 47.71 (2 C), 30.32 (2 C), 21.48.

The corresponding di(μ-acetato) complex was prepared from the chloride complex **47** according to the same procedure as for **37′**, from the corresponding chloride dimer: $^1$H NMR (200 MHz) δ 5.58 (br s, 1 H, H-3), 4.83 (br s, 2 H, H-2, H-4), 2.64 (br s, 2 H, H-1, H-5), 2.00 (s, 3 H, AcO), 1.52–1.20 (m, 6 H).

**Reactions with Preformed $\eta^3$-Allylpalladium Complexes, General Procedure.** The di(μ-acetato)$\eta^3$-allyl complex was treated with benzoquinone in acetic acid at 25 °C, with the concentrations of all reactants similar to those used in the catalytic procedure. Workup (as in general catalytic oxidation procedure A) provided the expected acetate isomers (see text) in generally good yields as determined by GLC. The identities of the products were confirmed by comparison with known samples ($^1$H NMR and GLC).

**Acetoxylation of Di(μ-chloro)bis[(1,2,3-η)-inden-1-yl]dipalladium (61).** A slurry of di(μ-chloro)bis[(1,2,3–η)inden-1-yl]dipalladium (129 mg, 0.5 mmol), benzoquinone (216 mg, 2 mmol), and AgOAc (116 mg, 2 mmol) was stirred in 25 mL of acetic acid at room temperature. After 2 h the solvent was removed in vacuo. The residue was suspended in 100 mL of diethyl ether and washed twice with 50 mL of 2 M NaOH and finally with 50 mL of water. The organic phase was dried over anhydrous $MgSO_4$, followed by filtration and evaporation of the solvent; crude yield ca. 70% (estimated from NMR). The product was purified by flash chromatography (eluent hexane–diethyl ether, 9:1), yield 40 mg (46%) of pure **17**.

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**Registry No.** 1, 20657-21-0; 2, 14447-34-8; 3, 826-13-1; 4, 31059-36-6; 5, 124021-30-3; 6, 1142-14-9; 7, 124021-31-4; 8, 124021-32-5; 9, 57031-79-5; 10, 124021-33-6; 11, 124021-34-7; 12, 92984-84-4; 13, 53723-45-8; 14, 53723-44-7; 15, 124021-35-8; 16, 124021-36-9; 17, 35116-20-2; 18, 13295-90-4; 19, 75411-49-3; 20, 124021-39-2; *cis*-21, 124021-37-0; *trans*-21, 124021-38-1; *cis*-22, 61221-47-4; *trans*-22, 61221-48-5; 23, 63382-59-2; 24, 74408-54-1; 25, 60729-56-8; 26, 124021-40-5; 27, 55591-27-0; 28, 55591-26-9; 29, 99572-30-2; 30, 124021-41-6; 31, 124021-42-7; 37, 96981-64-5; 37′, 124042-09-7; 47, 124021-43-8; 47′, 124021-44-9; 52, 4065-80-9; 53, 53723-50-5; 54, 20461-30-7; 55, 21378-21-2; 56, 32363-86-3; 57, 17488-64-1; 58, 18325-75-2; 59, 90112-22-4; 60, 932-89-8; 61, 90624-27-4; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; (*Z*)-cyclodecene, 935-31-9; (*E*)-cyclododecene, 1486-75-5; (*E*,*E*,*E*)-1,5,9-cyclododecene, 4904-61-4; (*E*)-3-hexene, 13269-52-8; (*E*)-5-decene, 7433-56-9; palladium diacetate, 3375-31-3; 1-methylcyclopentane, 693-89-0; *cis*-bicyclo[3.3.0]oct-1-ene, 930-99-4; indene, 95-13-6; 1-methylcyclohexene, 591-49-1; 3-methyl-1-cyclohexene, 591-48-0; 4-methyl-1-cyclohexene, 591-47-9; 1-phenylcyclohexene, 771-98-2; methyl 3-cyclohexenecarboxylate, 6493-77-2; 3-cyclohexene-1-carbonitrile, 100-45-8; 3-acetylcyclohexene, 7353-76-6; methylenecyclohexane, 1192-37-6; ethylidenecyclohexane, 1003-64-1; 1,5-dimethylcyclooct-1,5-diene, 3760-14-3; 1,6-dimethylcyclooct-1,5-diene, 3760-13-2.

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