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Palladium-catalyzed allylic acetoxylation: an exploratory study of the influence of added acids

Björn Åkermark, Sverker Hansson, Tobias Rein, Jan Vågberg,
Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm (Sweden)

Andreas Heumann
Faculté de St.-Jérôme-ESIPSOI, UA 126, F 13397 Marseille Cedex 13 (France)

and Jan-Erling Bäckvall
Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala (Sweden)
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Abstract

In order to investigate the possibility of improving the selectivity in palladium-catalyzed acetoxylation of substituted cycloalkenes and linear alkenes, the influence of added strong acids has been studied. It was found that the product selectivity can be increased in some cases, but also that side reactions lower the total yields when trifluoroacetic or stronger acids are used. The improvement of the selectivity may possibly be due to a change in mechanism for the acetoxylation.

Introduction

Allylic acetates are useful intermediates in organic synthesis since they will undergo a variety of transformations, either via the corresponding allylic alcohols or directly by metal catalyzed displacement of acetate by other nucleophiles [1]. A large number of procedures for the metal catalyzed preparation of allylic acetates from simple olefins have therefore been developed [2]. One of these procedures involve the use of palladium(II) as a catalyst. Owing to low yields and the formation of complex mixtures of products [3], this reaction has not found much use in organic synthesis. However, we have recently shown that unsubstituted cycloalkenes are efficiently and selectively converted into allylic acetates when palladium acetate is used as catalyst and a combination of benzoquinone and manganese dioxide as oxidant [4]. Independently, a similar oxidation–acetoxylation procedure involving palladium trifluoroacetate as catalyst and benzoquinone as oxidant was developed by McMurry [5].

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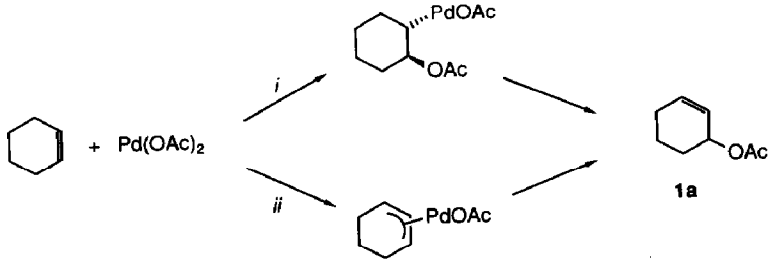
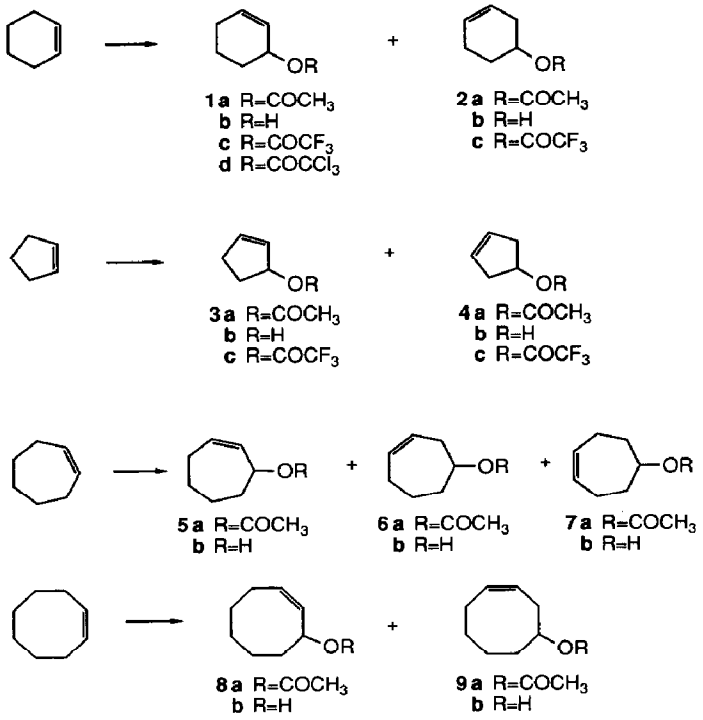
While total yields are high also in the acetoxylation of substituted cycloalkenes and linear alkenes, these reactions generally give mixtures of products [5,6a]. In agreement early mechanistic findings by Henry [7] and Wolfe [8], a reason for this low selectivity, could be that the acetoxylation products are formed through two competing pathways: (i) 1,2-acetoxypalladation followed by β-hydride elimination, and (ii) formation of a η^3-allyl complex followed by nucleophilic addition of acetate (Scheme 1). Since the properties of the palladium catalyst might affect the balance between the two postulated reaction paths, we decided to study the effect of addition of strong acids to the reaction medium, and the results are presented here.



Scheme 1

Results and discussion

The catalytic acetoxylation of several cyclic alkenes was performed in acetic acid over a fairly wide range of acidity determined by addition of small amounts of



Scheme 2

stronger acids such as trifluoroacetic and methanesulfonic acid. The results are summarized in Tables 1, 2 and 3. As expected, the presence of strong acids generally increases the rate of acetoxylation, but also complicates the reaction by promoting the formation of homoallylic acetates (Scheme 2). However, in a few cases increased selectivity was observed.

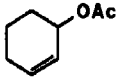
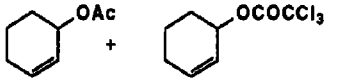
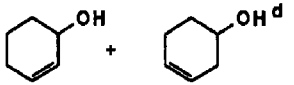
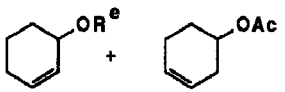
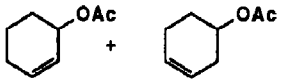
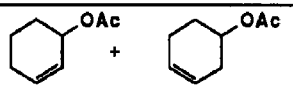
When cyclohexene is acetoxylated with palladium acetate as a catalyst and excess benzoquinone as oxidant, the acetoxylation to give **1a** requires about 47 h at 20 °C for completion [6a]. The addition of 1 equiv. of trichloroacetic acid has essentially no effect on the rate, but with 1 equiv. of trifluoroacetic acid the time required for completion is reduced to 27 h at 20 °C, and with 0.5 equiv. of methanesulfonic acid to 5 h at 20 °C, is essentially the same time as required with 5 equiv. of trifluoroacetic acid (Table 1).

Cyclopentene reacts faster at 20 °C when 1 equiv. of trifluoroacetic acid is added than at 60 °C in acetic acid alone. Similar trends are observed with cycloheptene and cyclooctene (Table 2). Addition of the strongest acid, methanesulfonic acid, leads to much lower yields for all the three cycloolefins, cyclopentene (7%), cycloheptene (26%) and cyclooctene (< 10%). Control experiments indicated that a major reason is that the allylic esters are rapidly consumed by further reactions when the reaction medium is too acidic. With added trichloroacetic and trifluoroacetic acid, the anions of these acids compete with acetate because the acids give anions essentially quantitatively through the equilibrium with acetate. For instance, considerable amounts of the trifluoroacetate **1c** are formed from cyclohexene (entry 4, Table 1).

There is also a more profound change in the product pattern as the acidity of the medium is increased; this involves the formation of homoallylic carboxylates and other products from double bond isomerization. Cyclohexene, for instance, gave > 98% of allylic acetate in the absence of added acids (entry 1, Table 1). In the presence of trifluoroacetic acid (5 equiv.), 6% homoallylic acetate **2a** was formed. Upon addition of 0.5 equiv. of methanesulfonic acid, the ratio of homoallylic to allylic acetate increased to 79/21, and when 1.1 equiv. were added the homoallylic acetate was the exclusive product. The yield is fairly low (50%), but a substantial and useful alteration of the product pattern has been achieved. Unfortunately, similar selectivity was not obtained with the other cycloalkenes, except for cyclopentene, and in this case the yield of **4a** was only 7% (entry 3, Table 2) owing to further reactions of the primary products such as were observed in the case of other alkenes.

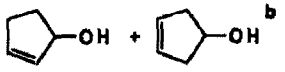
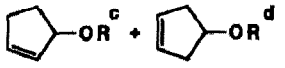
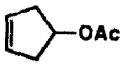
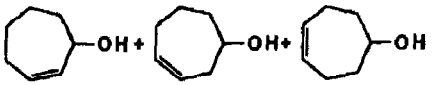
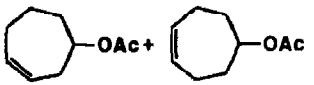
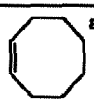
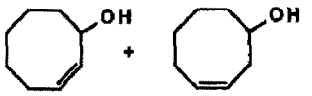
Since selectivity control is particularly interesting (and difficult) with substituted cycloalkenes and non-cyclic alkenes, the acetoxylation of 1-methylcyclohexene and *E*-3-hexene was also briefly investigated. When 1-methylcyclohexene was reacted in acetic acid in the absence of strong acids, approximately equal amounts of the isomeric acetates **10a** and **11** were formed (Scheme 3) [6a]. Upon addition of 1 equiv. of trichloroacetic acid (based on 1-methylcyclohexene), 2-methyl-2-cyclohexene-1-yl acetate (**10a**) became the sole product (entry 1, Table 3). Control experiments showed that acetate **11** undergoes further reactions more rapidly than **10a**, but the fair yield of **10a**, ca. 35%, suggests that considerable selectivity has been obtained in the acetoxylation process. Acetoxylation in the presence of trifluoroacetic acid also gave 2-methyl-2-cyclohexene-1-yl carboxylates **10** as the major products, and none of the isomers **11**. In addition, small amounts of 2-methylene-

Table 1. Oxidation of cyclohexene

Entry	Substrate	Products	Ratio	$Pd(OAc)_2$ %	Added acid %	Benzoquinone %	Temp	Time	Total yield %
1	 [a]	 1a	[b]	5	-	200	RT	16h	48
			[b]	5	-	200	RT	47h	86
2	—,,—	 1a + 1d	60:40 [c]	5	CCl_3CO_2H, 100	200	RT	49h	63
3	—,,—	 [d] 1b + 2b	98:2	5	CF_3CO_2H, 100	200	RT	27h	65
4	—,,—	 [e] 1a+1c + 2a	94:6	5	CF_3CO_2H, 500	200	RT	5h	60
5	—,,—	 1a + 2a	21:79	5	CH_3SO_3H, 50	200	RT	4.5h	62
6	—,,—	 1a + 2a	2:98	5	CH_3SO_3H, 110	200	50° C	75min	50

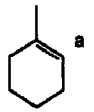
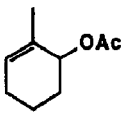
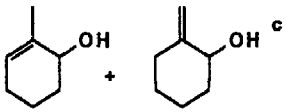
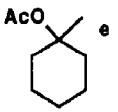
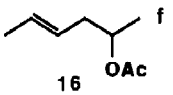
[a] The oxidation without added strong acids will be described in detail in a forthcoming paper [6]. [b] 98% pure isomer according to capillary GLC. [c] No homoallylic isomers detected by capillary GLC. [d] The initial products, a mixture of acetates and trifluoroacetates, were hydrolysed and isolated as the alcohols. [e] CH_3CO/CF_3CO 4/1.

Table 2. Oxidation of cyclopentene, cycloheptene, and cyclooctene

Entry	Substrate	Products	Ratio	$Pd(OAc)_2$ %	Added acid %	Benzoquinone %	Temp	Time	Total yield %
1	 [a]	 3b + 4b [b]	94:6	5	CF_3CO_2H, 100	200	RT	7h	59
2	—"—	 3a+3c + 4a+4c [c,d]	94:6	5	CF_3CO_2H, 500	200	RT	2h	60
3	—"—	 4a	e	5	CH_3SO_3H, 10 [f,g]	200	RT	2.5h	7
4	 [a]	 5b + 6b + 7b	84:9:7	5	CF_3CO_2H, 100	200	RT	54h	70
5	—"—	 6a + 7a	56:44	5	CH_3SO_3H, 100	200	RT	23h	26
6	 [a]	 8b + 9b	97:13	5	CF_3CO_2H, 100	200	RT	168h	16
7	—"—	h	h	5	CH_3SO_3H, 100	200	RT	69h	h

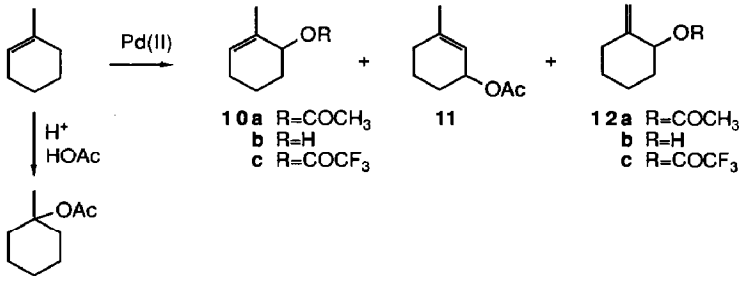
[a] The oxidation without added strong acids will be described in detail in a forthcoming paper [6]. [b] The initial products, a mixture of acetates and trifluoroacetates, were hydrolysed and isolated as the alcohols. [c] R = CH_3CO/CF_3CO 3/1. [d] R = CH_3CO/CF_3CO 2/1. [e] ≥ 95% isomeric purity as indicated by capillary GLC. [f] With 100% CH_3SO_3H added, the unsaturated acetates decompose very quickly. [g] The allylic acetate decomposes much faster than the homoallylic under these conditions. [h] ≤ 10% of unsaturated acetates formed as indicated by capillary GLC.

Table 3. Oxidation of 1-methylcyclohexene and 3-hexene

Entry	Substrate	Products	Ratio	$Pd(OAc)_2$ %	Added acid %	Benzoquinone %	Temp	Time	Total yield %
1	 a	 10a	b	5	CCl_3CO_2H, 100	200	50 °C	103h	35
2	—"—	 10b + 12b	90:8[d]	5	CF_3CO_2H, 100	200	RT	118h	32
3	—"—	 13	e	5	CH_3SO_3H, 100	200	RT	24h	35
4	 a	 16	f	5	CH_3SO_3H, 100	200	RT	2h	30

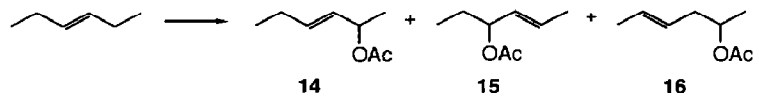
[a] The oxidation without added strong acids will be described in detail in a forthcoming paper [6]. [b] No other isomer as judged from ^1H NMR spectra. [c] The initial products, a mixture of acetates and trifluoroacetates, were hydrolysed and isolated as the alcohols. [d] < 2% of an unidentified isomer was also detected by capillary GLC. [e] Only trace amounts of unsaturated acetates formed. Control experiments showed that the main product was formed by acid catalyzed addition of HOAc to the olefin. [f] Contains approximately 20% of other isomers as indicated by capillary GLC (< 2% of allylic acetates).

cyclohex-1-yl products **12** were detected. Since the formation of product **12** via 1,2-acetoxypalladation (route i, Scheme 1) requires addition of palladium at the tertiary carbon of 1-methylcyclohexene, this route appears less probable. A route via an η^3-allyl complex (ii, Scheme 1) seems more likely under acidic reaction conditions. The mechanistic implications of this result have to be studied further.



Scheme 3

The experiments with 1-methylcyclohexene also show that in a very acidic medium, acid-catalyzed addition of acetic acid to the double bond competes with the palladium-catalyzed reaction. When acetoxylation was performed in the presence of methanesulfonic acid, the saturated ester 1-methylcyclohex-1-yl acetate (**13**) was the major product, accompanied by trace amounts of unsaturated acetates (entry 3, Table 3).



Scheme 4

The acetoxylation of *E*-3-hexene in acetic acid gave a 1/1 mixture of the acetates **14** and **15** (Scheme 4) [6]. This does not necessarily mean that the initial reaction is unselective since control experiments showed that under the reaction conditions, pure **14** and pure **15** were rapidly converted into a 1/1 mixture of both isomers [9]. Selective formation of one of the isomers is thus not possible. However, addition of methanesulfonic acid led to the formation of homoallylic acetate **16** as the main product (entry 4, Table 3). This means that reaction conditions can perhaps be found under which isomerization of the primary allylic acetates to the more stable homoallylic acetate is sufficiently rapid to compete with decomposition. An efficient and selective conversion of *E*-3-hexene to **16** would then be possible.

In conclusion, addition of strong acids increases the rate of acetoxylation and also changes the reaction pattern. The mechanistic implications of this change are not clear, but it is evident that useful selectivity may be obtained, for instance in the transformation of cyclohexene to the homoallylic acetate **2a** and 1-methylcyclohexene to 2-methyl-2-cyclohexene-1-yl acetate (**10a**).

Experimental

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. Pentane (Labassco, 95%) was distilled before use. Bulb-to-bulb distillation involved distillation in a Büchi GKR-50 Kugelrohr apparatus (oven temperatures are given in each case). Flash chromatography was performed as described by Still, Kahn and Mitra [10]. Analytical TLC was performed on Merck TLC Aluminium sheets F_{254} Silica gel 60, pre-coated, 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 δ 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 assignment of the products. GLC analysis was performed on a Varian 3700 instrument fitted with a BP-1 (methylsilicone, 25 m) capillary column, or a Pye Unicam GCD instrument (5% SE-30 on Chromosorb W as stationary phase). Reactions monitored by GLC were allowed to proceed until all starting material was consumed, or until there was no further increase in the amount of desired product. Elementary analyses were performed by Analytische Laboratorien, Engelskirchen, West Germany.

Experimental details for the oxidation of cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1-methylcyclohexene, and *E*-3-hexene to allylic acetates under optimized conditions without added strong acids will be given in a forthcoming paper.

Oxidation of cyclohexene, in the presence of CCl_3COOH (procedure A)

Cyclohexene (507 μl, 5.0 mmol) and undecane (250 μl, as internal standard) were added to a solution of $Pd(OAc)_2$ (56 mg, 0.25 mmol), Cl_3CCOOH (817 mg, 5.0 mmol) and benzoquinone (1081 mg, 10.0 mmol) in acetic acid (15 ml). The solution was stirred at room temperature and the progress of the reaction monitored by capillary GLC. After 48 h, the reaction was quenched by addition of ca. 1 g of anhydrous NaOAc. After a few minutes stirring the mixture was diluted with 50 ml of pentane/diethyl ether (1/1) and 20 ml of H_2O and filtered through Celite. The aqueous phase was extracted with 2×50 ml of pentane/ether (1/1), and the combined organic phases were washed with 2×20 ml of H_2O, 3×20 ml of saturated $NaHCO_3$ and 20 ml of brine. The solution was dried over $MgSO_4$ and filtered, and the solvent carefully evaporated on a rotary evaporator (water aspirator pressure, ambient temperature) to give ca. 1.08 g of a crude product mixture as a light yellow oil containing some precipitate. The ^1H NMR spectrum indicated that the main components were 2-cyclohexen-1-yl acetate (**1a**) and 2-cyclohexen-1-yl trichloroacetate (**1d**) in a 9/8 ratio. Flash chromatography (elution with a stepwise gradient of 1–10% ether in pentane) gave 305 mg (25%) of **1d** and 265 mg (38%) of **1a** as colourless oils. The ^1H NMR [11] and ^{13}C NMR [12] spectra of **1a** were in full agreement with those reported in the literature **1d**: ^1H NMR (400 MHz) δ 6.10 (dddd, $J = 10$, 4, 3, 1 Hz, 1H), 5.80 (ddt, $J = 10$, 4, 2.5 Hz, 1H), 5.39 (m, 1H), 2.28–1.62 (m, 6H); ^{13}C NMR (100 MHz) δ 161.53, 135.11, 123.21, 90.25, 73.79, 27.60, 24.79, 18.21. Identical spectra were recorded for a sample of **1d** prepared from **1a** by hydrolysis (KOH, MeOH, RT, 1.5 h) and reaction with trichloroacetic anhydride. Anal. Found: C, 39.36; H, 3.73; Cl, 43.80. $C_8H_9Cl_3O_2$ calc: C, 39.46; H, 3.73; Cl, 43.68%.

Oxidation of cyclohexene, in the presence of CF_3COOH (procedure B)

Cyclohexene (822 mg, 10 mmol) was added to a solution of $Pd(OAc)_2$ (112 mg, 0.5 mmol), *p*-benzoquinone (2.16 g, 20 mmol), and trifluoroacetic acid (1.14 g, 10 mmol) in acetic acid (30 ml). The mixture was stirred at 20 °C for 27 h and was then diluted with brine (10 ml) and 9/1 pentane/ether (50 ml). The mixture was filtered and the aqueous phase extracted with 9/1 pentane/ether (3 × 50 ml). The combined organic phases were washed with water (30 ml), sat. Na_2CO_3 (3 × 30 ml), water (30 ml), and brine (30 ml). The solution was dried over $MgSO_4$ and the solvents then removed by distillation at ambient pressure through a Vigreux column. The residual oil (2.13 g), containing a mixture of allylic and homoallylic acetates and trifluoroacetates, was dissolved in methanol (5 ml) and 2 *M* NaOH (10 ml) was added. The solution was stirred at 50 °C for 2 h and then allowed to cool to room temperature. After the addition of NaCl (1 g) the mixture was extracted with ether (4 × 40 ml). The extracts were washed with water (5 + 10 ml) and brine (5 ml) and the combined aqueous phases were extracted with ether (2 × 30 ml). The combined ether phases were dried over $MgSO_4$ and the solvent removed by distillation (Vigreux column, ambient pressure) to yield 734 mg of a colorless oil. Bulb-to-bulb distillation at 120 °C (1 mm Hg) gave 636 mg (65%) of 2-cyclohexen-1-ol (**1b**) and 3-cyclohexen-1-ol (**2b**) in a 98/2 ratio as determined by capillary GLC. The ^1H NMR spectra of **1b** [13–15] and **2b** [16] were in full agreement with those reported previously. **1b**: ^{13}C NMR (50 MHz, peaks assigned from spectrum of the mixture) δ 130.10, 129.89, 65.25, 31.79, 24.88, 18.89. **2b**: ^{13}C NMR (50 MHz, peaks assigned from spectrum of the mixture) δ 126.59, 124.01, 66.70, 34.15, 30.72, 23.61.

Oxidation of cyclohexene, in the presence of CH_3SO_3H (procedure C)

The reaction was carried out as described for procedure A (2 mmol scale, 50 °C, 75 min) but with CCl_3COOH in place of CH_3SO_3H (143 µl, 2.2 mmol). After the usual work-up (including flash chromatography), **2a** (142 mg; 50%) was obtained as a colourless oil. The ^1H NMR [17] and ^{13}C NMR [17] spectral data agreed with those in the literature. Capillary GLC analysis gave the isomeric ratio **2a**/**1a** as ≥ 85/1.

When the oxidation of cyclohexene was performed as above, but with 50 mol-% of CH_3SO_3H at room temperature for 4.5 h, a 79/21 mixture (according to ^1H NMR) of **2a** and **1a** was obtained (yield 62%).

Oxidation of cyclopentene according to procedure B

The reaction was performed as above on a 10 mmol scale at room temperature for 7 h. After the normal extractive work-up, hydrolysis (2 *M* NaOH, MeOH, 50 °C, 2.5 h) and bulb-to-bulb distillation at 80 °C (0.5–1 mm Hg), 499 mg (59%) of a colorless oil were isolated. According to ^1H NMR analysis [15,18,19] the oil consisted of a 94/6 mixture of 2-cyclopenten-1-ol (**3b**) and 3-cyclopenten-1-ol (**4b**). **3b**: ^1H NMR (200 MHz) δ 5.96 (ddt, J = 5.5, 2, 1 Hz, 1H), 5.82 (dq, J = 5.5, 2 Hz, 1H), 4.84 (m, $w_{1/2}$ = 13 Hz, 1H), 2.64 (br, s, 1H, D_2O exchangable), 2.49 (m, 1H), 2.24 (m, 2H), 1.68 (m, 1H); ^{13}C NMR (50 MHz) δ 134.67, 133.22, 77.18, 33.00, 30.82.

Oxidation of cyclopentene according to procedure C

This oxidation was performed as described for cyclohexene: 10 mmol scale, 10 mol-% (65 µl, 1.0 mmol) of CH_3SO_3H, decane as internal standard, room tempera-

ture, 2.5 h. After the usual extractive work-up (including washing of the organic phase with 2 *M* NaOH), removal of solvent distillation through a Vigreux column and finally bulb-to-bulb distillation (60–70 torr, 150 °C) gave 87 mg (7%) of **4a** as a colourless oil. ^{1}H NMR (400 MHz) δ 5.71 (m, 2 H), 5.36 (tt, J = 6.9, 2.4 Hz, 1H), 2.72 (br dd, J = 16.5, 6.9 Hz, 2H), 2.38 (br dd, J = 16.5, 2.3 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz) δ 170.96, 128.24, 74.15, 39.66, 21.27. According to capillary GLC, the isomeric purity of the product was $\geq$ 95%. The structure of the product was confirmed by hydrolysis (2 *M* NaOH, MeOH, RT, over night) to the known alcohol **4b**. The ^{1}H NMR and ^{13}C NMR data for **4b** agreed with those in the literature [19].

Oxidation of cycloheptene according to procedure B

The reaction was performed on a 10 mmol scale as described for cyclohexene; 54 h, room temperature. The usual work-up, hydrolysis (2 *M* NaOH, MeOH, 50 °C, 1.5 h) and bulb-to-bulb distillation at 110 °C (0.5 mm Hg) afforded 786 mg (70%) of an inseparable mixture of 2-cyclohepten-1-ol (**5b**), 3-cyclohepten-1-ol (**6b**), and 4-cyclohepten-1-ol (**7b**). The ratio, as determined by integration of the three separate signals for C*H*-OH in the ^{1}H NMR spectrum, was **5b**/**6b**/**7b** = 84/9/7. **5b**: ^{1}H NMR (200 MHz) δ 5.74 (m, 2 H), 4.39 (br d, J = 9.5 Hz, 1H), 2.23–1.82 (m, 4H), 1.76–1.30 (m, 5H); ^{13}C NMR (50 MHz, assigned peaks in mixture with **6b** and **7b**) δ 138.01, 129.60, 71.82, 36.51, 28.48, 26.77, 26.58. **6b**: ^{1}H NMR (200 MHz, distinguishable peaks in mixture with **5b** and **7b**) δ 5.95–5.89 (m, 1H), 5.66–5.59 (m, 1H), 3.70 (m, 1H). **7b**: ^{1}H NMR (200 MHz, distinguishable peaks in mixture with **5b** and **6b**) δ 5.80–5.70 (m, 2H), 3.85 (tt, J = 9.0, 4.0 Hz, 1H). The identities of the three isomers were confirmed by comparison with ^{1}H NMR data in the literature [20–22].

Oxidation of cycloheptene according to procedure C

The oxidation was carried out as described for cyclohexene (5 mmol scale) 100 mol-% (325 μl, 5 mmol) of CH_3SO_3H, undecane as internal standard, room temperature, 23 h) and gave 184 mg (26%) of an inseparable mixture of **6a** and **7a** after the usual extractive work-up followed by flash chromatography. **6a**: ^{1}H NMR (400 MHz, assigned from spectrum of the mixture) δ 5.91–5.85 (m, 1H), 5.63–5.57 (m, 1H), 4.69 (tt, J = 9.6, 3.4 Hz, 1H), 2.43–2.27 (m, 2H), 2.16–1.94 (m, 3H), 2.00 (s, 3H), 1.75–1.65 (m, 2H), 1.45–1.35 (m, 1H); ^{13}C NMR (100 MHz, assigned from spectrum of the mixture) δ 170.36, 134.41, 125.49, 72.12, 37.31, 34.06, 28.30, 23.64, 21.43. **7a**: ^{1}H NMR (400 MHz, assigned from spectrum of the mixture) δ 5.80–5.72 (m, 2H), 4.94 (tt, J = 8.7, 4.6 Hz, 1H), 2.27–2.16 (m, 2H), 2.16–1.94 (m, 2H), 2.02 (s, 3H), 1.91–1.94 (m, 2H), 1.60–1.52 (m, 2H); ^{13}C NMR (100 MHz, assigned from spectrum of the mixture) δ 170.36, 131.63, 75.93, 32.10, 23.01, 21.43. The ^{1}H NMR signal assignments were confirmed by extensive decoupling experiments. According to ^{1}H NMR, the ratio **6a**/**7a** was 56/44. Comparison with the ^{1}H NMR spectrum of an authentic sample [11] revealed that there were no detectable amounts of **5a** in the product.

Hydrolysis (2 *M* NaOH, MeOH, RT, over night) of the mixture of acetates afforded the two known alcohols **6b** and **7b** in the same ratio. The ^{1}H NMR data agreed with those published [21,22]; ^{13}C NMR (100 MHz, assigned from spectrum of the mixture): **6b** δ 134.75, 125.91, 69.13, 40.83, 37.30, 28.33, 23.21; **7b** δ 131.81, 74.05, 35.57, 22.91.

Oxidation of cyclooctene according to procedure B

The reaction was carried out on a 10 mmol scale for 168 h at room temperature. After the usual work-up and hydrolysis (2 *M* NaOH, MeOH, 50 °C, 2 h) the crude oil was distilled in a bulb-to-bulb apparatus. Two fractions were collected. The first fraction at 55 °C (1 mm Hg), gave 471 mg (43%) of unchanged cyclooctene. A second fraction, at 125 °C (0.5 mm Hg), afforded 207 mg (16%) of a colorless oil, which consisted of 2-cycloocten-1-ol (**8b**) and 3-cycloocten-1-ol (**9b**) in a 87/13 ratio as indicated by capillary GLC. The identity of the major product was established by use of published ^{1}H NMR data [23]. The ^{1}H and ^{13}C NMR data of **9b** were in full agreement with those reported previously [24,25]. Neither the ^{1}H NMR nor the ^{13}C NMR spectrum showed any trace of the third possible isomer, 4-cycloocten-1-ol [15,22].

8b: ^{13}C NMR (50 MHz, peaks assigned from spectrum of mixture with **9b**) δ 135.00, 128.45, 69.32, 38.55, 29.12, 26.25, 26.07, 23.66.

Attempted oxidation of cyclooctene according to procedure C

When oxidation of cyclooctene (2 mmol) was attempted by the method described for cyclohexene (100 mol-% CH_3SO_3H, dodecane as internal standard), GLC analysis indicated that $\leq 10\%$ of unsaturated acetates (**8a** used as reference) had been formed after 69 h at room temperature (ca. 25% conversion of cyclooctene). No isolation or further characterization of the products was attempted.

Oxidation of 1-methylcyclohexene according to procedure A

This reaction was performed on a 2 mmol scale in the way described for oxidation of cyclohexene (50 °C, 103 h, decane as internal standard). The same work-up procedure, including flash chromatography, afforded 109 mg (35%) of **10a** as a colourless oil. ^{1}H NMR (400 MHz) δ 5.66 (m, 1 H), 5.19 (br t, $J = 5$ Hz, 1H), 2.12–1.88 (m, 2H), 2.05 (s, 3H), 1.78–1.74 (m, 2H), 1.63 (br s, 3H), 1.64–1.50 (m, 2H); ^{13}C NMR (100 MHz) δ 170.99, 131.64, 127.84, 70.66, 28.85, 25.09, 21.25, 20.40, 18.28. Identical spectra were recorded for a sample of **10a** prepared from the corresponding known alcohol **10b** [15,26].

Oxidation of 1-methylcyclohexene according to procedure B

1-Methylcyclohexene was oxidized by the standard procedure (10 mmol scale, 118 h, room temperature). After hydrolysis (2 *M* NaOH, MeOH, 50 °C, 2 h) and bulb-to-bulb distillation at 140 °C (1 mm Hg), 360 mg (32%) of a colorless oil were isolated. According to ^{1}H and ^{13}C NMR analysis the oil consisted of a 90/8 mixture of 2-methyl-2-cyclohexen-1-ol (**10b**) [15,26,27] and 2-methylenecyclohexan-1-ol (**12**) [13,15]. Less than 2% of an unidentified isomer was also detected by capillary GLC.

Oxidation of E-3-hexene according to procedure C

Performing the oxidation as described for cyclohexene (2 mmol scale, 100 mol-% (130 μl, 2 mmol) CH_3SO_3H, n-decane as internal standard), at room temperature for 2 h, gave, after the usual extractive work-up followed by flash chromatography, 85 mg (30%) of a 4/1 mixture of two unsaturated acetates. The structure of the major product **16** was confirmed by comparing its GLC retention time and ^{1}H and NMR and ^{13}C NMR data with those of sample prepared by oxidation of 1-hexene

with a stoichiometric amount of $PdCl_2$ [28]. ^1H NMR (200 MHz) δ 5.60–5.30 (m, 2H), 4.89 (app sext, $J = 6.3$ Hz, 1H), 2.43–2.05 (m, 2H), 2.03 (s, 3H), 1.66 (d, $J = 5.9$ Hz, 3H), 1.19 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (50 MHz) δ 169.48, 127,49, 125.54, 70.29, 34.09, 21.12, 17.78, 13.94.

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References

1 (a) B.M. Trost, Acc. Chem. Res., 13 (1980) 385; (b) B.M. Trost and T.J. Verhoeven, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, Oxford, 1982, p. 799 ff; (c) J. Tsuji, Organic Synthesis with Palladium Compounds, Springer-Verlag, Berlin, 1980.
2 See e.g. J. Muzart, Bull. Chim. Soc. France, (1986) 65, and references cited therein.
3 For a recent review see P.M. Henry, Palladium Catalyzed Oxidation of Hydrocarbons, D. Reidel Publishing Co, Dordrecht, 1980, pp. 84–126.
4 A. Heumann and B. Åkermark, Angew. Chem., Int. Ed. Engl., 23 (1984) 453.
5 J.E. McMurry and P. Kocovsky, Tetrahedron Lett., 25 (1984) 4187.
6 (a) B. Åkermark, A. Heumann, S. Hansson, and T. Rein, to be published; (b) A. Heumann, S. Hansson, T. Rein, and B. Åkermark, Org. Synth., in press.
7 P.M. Henry and G.A. Ward, J. Am. Chem. Soc., 93 (1971) 1494.
8 S. Wolfe and P.G.C. Campbell, J. Am. Chem. Soc., 93 (1971) 1497, 1499.
9 This reaction is obviously a palladium(II)-catalyzed rearrangement. For a review, see L.E. Overman, Angew. Chem., Int. Ed. Engl., 23 (1984) 579. Cf. also P.M. Henry, Acc. Chem. Res., 6 (1973) 16.
10 W.C. Still, M. Kahn, and A. Mitra, J. Org. Chem., 43 (1978) 2923.
11 A.J. Pearson and S.Y. Hsu, J. Org. Chem., 51 (1986) 2505.
12 Y.L. Chow and G.E. Buono-Core, J. Am. Chem. Soc., 108 (1986) 1234.
13 G.A. Kraus and K. Frazier, J. Org. Chem., 45 (1980) 2579.
14 A.J. Baggaley and R. Brettle, J. Chem. Soc. (C), 16 (1968) 2055.
15 K. Blau, U. Müller, W. Pritzkow, W. Schmidt-Renner, and Z. Sedshaw, J. Prakt. Chem., 322 (1980) 915.
16 R. Brettle and J.R. Sutton, J. Chem. Soc., Perkin Trans. 1, 19 (1975) 1947.
17 J.B. Lambert and D.E. Marko, J. Am. Chem. Soc., 107 (1985) 7978.
18 A. Maercker and R. Geuß, Chem. Ber., 106 (1973) 773.
19 S.E. Cremer and C. Blankenship, J. Org. Chem., 47 (1982) 1626.
20 S. Uemura and S. Fukuzawa, J. Am. Chem. Soc., 105 (1983) 2748.
21 E.A. Hill, R.J. Theissen, C.E. Cannon, R. Miller, R.B. Guthrie, and A.T. Chen, J. Org. Chem., 41 (1976) 1191.
22 J.K. Crandall, D.B. Banks, R.A. Colyer, R.J. Watkins, and J.P. Arrington, J. Org. Chem., 33 (1968) 423.
23 C.B. Reese and A. Shaw, J. Chem. Soc., Perkin Trans. 1, 23 (1975) 2422.
24 A.J. Bloodworth, J.A. Khan, and M.E. Loveitt, J. Chem. Soc., Perkin Trans. 1, 2 (1981) 621.
25 K.B. Wiberg and J. Pfeiffer, J. Am. Chem. Soc., 92 (1970) 553.
26 T. Ishida, Y. Asakawa, M. Okana, and T. Aratani, Tetrahedron Lett., (1977) 2437.
27 Y. Senda, S. Imaizumi, S. Ochiai, and K. Fujita, Tetrahedron, 30 (1974) 539.
28 O.G. Levanda and I.I. Moiseev, Zh. Org. Khim., 4(9) (1968) 1533 (Russ).