Acta Chemica Scandinavica, 1997: 51: 773–777
Printed in UK – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Application of O_2–DMSO as Reoxidant in the Pd(II)-Catalyzed 1,4-Oxidation of 5-Substituted 1,3-Cyclohexadienes

Magnus Rönn, Pher G. Andersson* and Jan-E. Bäckvall*

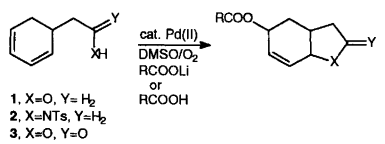
Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Rönn, M., Andersson, P. G. and Bäckvall, J.-E., 1997. Application of O_2–DMSO as Reoxidant in the Pd(II)-Catalyzed 1,4-Oxidation of 5-Substituted 1,3-Cyclohexadienes. – Acta Chem. Scand. 51: 773–777. © Acta Chemica Scandinavica 1997.

Palladium-catalyzed oxidation of 5-substituted 1,3-cyclohexadienes carrying a nucleophilic group in the side chain employing O_2–DMSO as the oxidant gave cyclization via 1,4-addition to the 1,3-diene. The nucleophilic groups employed were tosylamido and carboxy. In the reaction Pd^{II} is most likely reduced to colloidal Pd^0, which is subsequently reoxidized by O_2. The solvent DMSO prevents precipitation of metallic palladium by coordination to the colloidal particles. The stereochemistry of the palladium-catalyzed intramolecular 1,4-oxidation was controlled to some extent by the nature of the external nucleophile. Thus, in the intramolecular 1,4-oxyacyloxylation of **1** (hydroxy as nucleophile in the side chain) it was possible to direct the 1,4-addition towards *cis* or *trans* stereochemistry by variation of the external carboxylate nucleophile.

Palladium-catalyzed oxidations of olefins and dienes are of current interest in synthetic organic chemistry.[1–3] The potential use of these reactions in industrial applications has led to the search for improved and inexpensive reoxidation systems. Recently, a number of new palladium-catalyzed oxidations of alkenes and dienes based on the use of molecular oxygen have been developed.[4–7]

The oxidation system O_2 in DMSO has recently been successfully used in the palladium-catalyzed oxidation of alkenes.[5–7] In connection with our studies on palladium-catalyzed oxidation of conjugated dienes[1,4,8] it was of interest to apply the O_2–DMSO system to these reactions. In this account we report on the use of O_2–DMSO as a reoxidant for palladium in intramolecular 1,4-additions of the 1,3-dienes **1**, **2** and **3** (Scheme 1). An interesting observation is that the stereochemistry of the 1,4-addition depends on whether a carboxylic acid or its lithium salt is employed as the external nucleophile.



Scheme 1. Pd-catalyzed 1,4-oxidation by O_2 in DMSO.

* To whom correspondence should be addressed.

Results and discussion

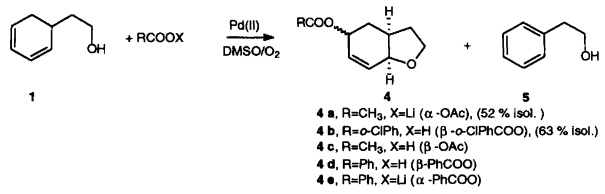
Optimization of the stereochemistry in the oxyacyloxylation. Reaction of **1**. Palladium-catalyzed oxidation of the diene alcohol **1** in DMSO by molecular oxygen in the presence of different carboxylic acids was studied. The catalyst used was palladium acetate. This reaction produces 5-acyloxy-substituted hexahydrobenzofurans **4** together with some isomerized starting material. An important aspect of this reaction is the stereochemistry of the 1,4-addition over the 1,3-diene which, using *p*-benzoquinone as reoxidant, earlier was controlled by the concentration of chloride ion. As even small amounts of halide ion inhibit the reaction with O_2–DMSO as reoxidant other reaction conditions and additives were examined. It was found that the stereochemical outcome of the addition is strongly dependent on the nature of the external nucleophile. Thus, the use of a salt of the carboxylic acid gave the 1,4-*trans* addition product (>95% *trans*) whereas the use of the carboxylic acid itself favored the formation of the 1,4-*cis* addition product (Scheme 2, Table 1). Reaction of **1** in the presence of LiOAc in DMSO under 1 atm of O_2 produced **4a** (>95% 1,4-*trans* addition) together with some aromatized starting material **5**, the ratio **4a**:**5** being 4:1 (Table 1, entry 1 and 3). The isolated yield of **4a** after work-up was 52%. An increase in temperature gave essentially the same result with a shorter reaction time. The use of lithium benzoate as the external nucleophile gave the

Table 1. Variation of carboxylic acid and salt to control the 1,4-*cis*: 1,4-*trans* selectivity.

Entry	RCOOX	*cis*: *trans*[a]	Major product **4**	**4**:**1**:**5**[b]	Conditions
1	AcOLi	<5:95	**4a**	80:0:20	48 h RT
2	AcONa	<5:95	**4a**	65:15:20	48 h RT
3	AcOLi	<5:95	**4a**	80:0:20	24 h 40 °C
4	PhCOOLi	<5:95	**4e**	65:10:25	24 h 40 °C
5	AcOH	50:50	**4a**,**4c**	70:17:13	24 h 40 °C
6	PhCOOH	90:10	**4d**	34:23:43	36 h 40 °C
7	*o*-ClC_6H_4COOH	93:7	**4b**	83:0:17	18 h 40 °C
8	*o*-ClC_6H_4COOH	93:7	**4b**	87:0:13	48 h RT
9	*o*-ClC_6H_4COOH	94:6	**4b**	86:7:7	24 h RT
10	2,4-$Cl_2PhCOOH$	90:10		85:5:15	48 h RT
11	2,4-$Cl_2PhCOOH$	80:20		58:0:42	24 h 40 °C
12	*p*-ClC_6H_3COOH	90:10		46:15:39	24 h RT
13	*p*-FC_6H_4COOH	88:12		78:14:8	24 h RT
14	*o*-BrC_6H_4COOH	94:6		81:8:11	24 h RT

[a]The *cis*: *trans* ratio was determined using ^1H NMR integrals over the allylic bridge head protons. The data of the acetate adducts were compared with those reported in the literature. The aroyloxy adducts were hydrolyzed to the corresponding alcohols **10** and **11**. [b]Determined using the ^1H NMR integrals of the crude product.

same stereoselectivity but a lower conversion and slightly more aromatic product **5** (entry 4). For acetic acid the selectivity 1,4-*cis*: 1,4-*trans* was only 50:50 (entry 5) but the selectivity for 1,4-*cis* addition increased with the strength of the acid and was 90:10 for benzoic acid (entry 6) and 93:7 for *o*-chlorobenzoic acid (entries 7 and 8, Table 1).

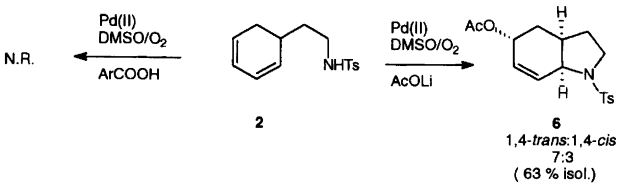


Scheme 2. Controlling the stereochemistry of the 1,4-addition over the 1,3-diene.

Attempts to use *p*-nitrobenzoic acid as the external nucleophile gave no reaction and the use of *p*-methoxybenzoic acid gave a very slow reaction.

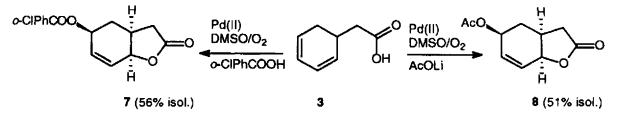
Reaction of **2**. The successful control of the 1,4-*cis*: 1,4-*trans* selectivity with diene **1** encouraged us to try other dienes. In the case of cyclization of tosylamide **2**[9] the selectivity for 1,4-*trans* addition with LiOAc as the external nucleophile was lower than for **1**. Thus **6** was obtained as a 7:3 mixture of 1,4-*trans* and 1,4-*cis* addition products. The use of *o*-chlorobenzoic acid as the external nucleophile did not result in any product possibly due to the low nucleophilicity of the nitrogen at this lower pH (Scheme 3).

Reaction of **3**. Palladium-catalyzed oxidation of diene acid **3** employing *o*-chlorobenzoic acid as the external nucleophile resulted in 1,4-*cis* addition over the diene to give lactone **7** (>95% 1,4-*cis* addition). Surprisingly, change of the external nucleophile to lithium acetate did not give the expected 1,4-*trans* addition in this case but



Scheme 3. Reactivity of the amide **2**.

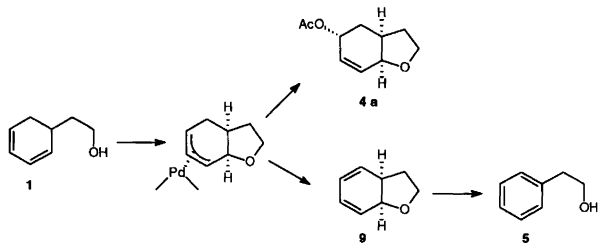
afforded lactone **8** via a 1,4-*cis* addition (Scheme 4). The reason for the difference between **1** and **3** in the reaction with lithium acetate is not clear. The high selectivity for 1,4-*cis* acyloxylactonization is interesting in the light of the moderate selectivity of the previous Pd-catalyzed procedure for this transformation. The present method is a major improvement over the previous method where the best result in the acyloxylactonization was 75% *cis* addition.[8c,10]



Scheme 4. Reactivity of the acid **3**.

Mechanistic considerations. A side reaction in these 1,4-oxidation reactions is the aromatization of the starting diene. This aromatization could in principle take place directly from **1** but it is more likely that it proceeds via diene **9**. Diene formation from (π-allyl)palladium complexes is well known[11–13] and formation of diene **9** followed by *anti* elimination of a hydrogen and the oxygen function would give **5** (Scheme 5). A possible explanation of the higher proportion of aromatized product in the O_2–DMSO reaction compared to the 1,4-benzoquinone–HOAc reactions is that the attack by the external nucleophile (e.g., AcO^-) on the intermediate

(π-allyl)palladium complex is slower with the former system.[14] As a consequence, the competing β-hydride elimination occurs to a larger extent. A change in temperature did not significantly change the ratio between 1,4-oxidation product and aromatized starting material.



Scheme 5. Possible mechanism for aromatization of **1**.

The mechanism of palladium-catalyzed oxidations with the O_2–DMSO system has been discussed and considered to involve colloidal palladium(0).[5b,5c,15] The role of DMSO would then be to dissolve such cluster-like particles.[16] It is well known that sulfoxides coordinate to palladium(II)[17] and the fact that they act as rate-accelerating ligands in palladium(II)-catalyzed reactions[4b] may also play an important role. The coordination properties of the DMSO may help to stabilize colloidal palladium by coordination to individual atoms in the cluster.

Conclusions. In conclusion, this newly developed method offers an inexpensive and environmentally safe reoxidation system. It is general, selective and in some cases this new method leads to an improvement of the stereoselectivity compared with the previous methods reported. An interesting aspect of the present procedure is that it can be run at a higher pH than the corresponding benzoquinone-promoted palladium-catalyzed 1,4-oxidations.[4,8] The latter oxidation system requires a weakly acidic solution whereas, with the present oxidation system (O_2–DMSO), the reaction tolerates a wider pH range and allows weakly basic conditions.

Experimental

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were run on a Varian Unity 400 spectrometer. $CDCl_3$ was used as the solvent unless otherwise stated, and the chloroform signal at 7.26 ppm (for ^1H) or 77.0 ppm (for ^{13}C) was used as the reference. IR spectra were obtained for thin films or $CDCl_3$ solutions on a Perkin–Elmer 1600 FT-IR instrument, and only the strongest/structurally most important peaks are listed. Merck silica gel 60 (240–400 mesh) was used for flash chromatography. The synthesis of the dienes **1**,[18] **2**[9] and **3**[10] were made according to known literature procedures. Compounds **10** and **12** were characterized by comparison with authentic samples prepared from the known acetates **4a**[8b] and **8**[8c] by hydrolysis. Compound **11** was acetylated to give the corresponding known acetate **4c**.[8b]

General procedure for palladium(II)-catalyzed cyclization of dienes. Method A. To the diene (1 mmol in 1 ml of DMSO), was added 8–12 equiv. of acid or the salt of an acid. The atmosphere was changed to oxygen by applying a vacuum immediately followed by inlet of O_2. This procedure was repeated once. The solution was stirred for 5 min, after which $Pd(OAc)_2$ (0.1 mmol) was added by opening the vessel while a slow stream of oxygen was maintained. Once again the vessel was evacuated followed by inlet of O_2. When the reaction was finished according to TLC, water (20 ml) was added and the product was extracted with pentane–ether 50:50 (3 × 15 ml). When an acid was used as second nucleophile the combined organic layers were washed once with Na_2CO_3(sat) (20 ml) to remove the acid. The organic phase was subsequently washed once with water (20 ml) and once with brine (20 ml) and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was examined by NMR spectroscopy.

When a salt was used as the external nucleophile the same work-up procedure was employed except for the Na_2CO_3 wash.

Method B. To 3 ml of dry DMSO was added 0.1 mmol of $Pd(OAc)_2$ and 6 equiv. of acid or the salt of an acid. The atmosphere was changed to molecular oxygen using the above described procedure. After 5 min the diene, 1 mmol, was added via a syringe.

Stereocontrolled oxyacyloxylation. Method A was used and the amount of external nucleophile was 8–12 equiv. The temperature and reaction time are indicated in Table 1. The same work-up as in Method A was used and the crude product was examined by ^1H NMR spectroscopy.

5-Acetoxy-2,3,3a,4,5,7a-hexahydro-(3aα,5α,7aα)-benzofuran (**4a**). Method B, 6 equiv. of LiOAc, was used and the same work-up as in Method A was employed. Compound **1** (248 mg, 2.00 mmol) gave **4a** (163 mg, 1.04 mmol, 52% yield, >95% *trans*) after flash chromatography in pentane–ether 75:25. The spectral data were in accordance with those reported in the literature.[8b]

5-(o-chlorobenzoyloxy)-2,3,3a,4,5,7a-hexahydro-(3aα,5β,7aα)-benzofuran (**4b**). Method B, 6 equiv. of *o*-chlorobenzoic acid, was used and the same work-up as in Method A was employed. Compound **1** (248 mg, 2.00 mmol) gave **4b** (348 mg, 1.26 mmol, 63% yield, 92:8 *cis*:*trans*) after flash chromatography in pentane–ether 50:50. R_f(pentane–ether 50:50) 0.53. ^1H NMR (400 MHz; $CDCl_3$): δ 7.80 (1 H, dd, J=7.8, 1.7 Hz), 7.42 (2 H, m), 7.30 (1 H, m), 6.00 (2 H, s), 5.53 (1 H, m), 4.11 (1 H, m), 4.03 (1 H, m), 3.82 (1 H, ddd, J=8.6, 8.5, 5.6 Hz), 2.47 (1 H, br), 2.22 (1 H, m), 2.13 (1 H, m), 1.77 (1 H, m), 1.64 (1 H, m). ^{13}C NMR (100 MHz; $CDCl_3$): δ 165.3, 133.7, 132.5, 131.3, 131.2, 131.0, 130.2, 128.2, 126.5, 73.6, 70.7, 67.2, 34.6, 32.2, 30.3. IR: ν_{max} (neat)/cm^{-1} 1730.

5-Benzoyloxy-2,3,3a,4,5,7a-hexahydro-(3aα,5β,7aα)-benzofuran (**4d**). Method B, 6 equiv. of benzoic acid, was used and the same work-up as in Method A was employed. Compound **1** (62 mg, 0.5 mmol) gave **4d** (55 mg, 0.23 mmol, 45% yield, 81:19 *cis*:*trans*) after flash chromatography in pentane–ether 75:25. R_f(pentane–ether 75:25) 0.35. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.04 (2 H, dd, J=8.4, 1.4 Hz), 7.56 (1 H, m), 7.44 (2 H, m), 6.00 (2 H, m), 5.52 (1 H, m), 4.13 (1 H, m), 4.05 (1 H, m), 3.84 (1 H, app dt, J=8.5, 5.6 Hz), 2.49 (1 H, m), 2.22 (1 H, m), 2.11 (1 H, m), 1.78 (1 H, m), 1.64 (1 H, app dt, J=12.4, 9.8 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ 166.1, 133.0, 131.6, 130.3, 129.6, 128.3, 128.1, 73.7, 69.9, 67.2, 34.7, 32.3, 30.5. IR: ν_{max} ($CDCl_3$)/cm^{-1} 1716.

5-Benzoyloxy-2,3,3a,4,5,7a-hexahydro-(3aα,5a,7aα)-benzofuran (**4e**). Method B, 6 equiv. of lithium benzoate, was used and the same work-up as in Method A was employed. Compound **1** (62 mg, 0.5 mmol) gave **4e** (59 mg, 0.24 mmol, 48% yield, >95% *trans*) after flash chromatography in pentane–ether 75:25. R_f(pentane–ether 75:25) 0.35. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.03 (2 H, m), 7.55 (1 H, m), 7.43 (2 H, m), 6.08 (2 H, m), 5.51 (1 H, m), 4.27 (1 H, dd, J=6.3, 2.7 Hz), 3.97 (1 H, app dt, J=8.2, 5.8 Hz), 3.81 (1 H, app dt, J=8.4, 6.4 Hz), 2.65 (1 H, m), 2.18 (1 H, m), 1.97 (2 H, m), 1.75 (1 H, m). ^{13}C NMR (100 MHz; $CDCl_3$): δ 166.0, 132.9, 131.1, 130.4, 129.6, 128.3, 128.3, 73.8, 66.9, 66.7, 33.3, 31.0, 30.1. IR: ν_{max} ($CDCl_3$)/cm^{-1} 1712.

Acetoxy tosylamide (**6**). Method B with 6 equiv. of LiOAc. The same work-up as in Method A was employed except that EtOAc was used to extract the product. Compound **2** (56 mg, 0.20 mmol) gave **6** (45 mg, 0.13 mmol, 63% yield, 1,4-*trans*:1,4-*cis*=7:3) after flash chromatography using pentane–Et_2O 1:1 as the eluent. The spectral data were in accordance with those reported in the literature.[9]

Lactone **7**. Method B, 6 equiv. of *o*-chlorobenzoic acid, was used. Work-up was done by evaporating the solvent off under reduced pressure. Compound **3** (69 mg, 0.50 mmol) gave **7** (81 mg, 0.28 mmol, 56% yield, >95% *cis*) after flash chromatography in pentane–ether 20:80. R_f(pentane–ether 20:80) 0.26. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.80 (1 H, ddd, J=7.6, 2.1, 0.6 Hz), 7.45 (2 H, m), 7.33 (1 H, ddd, J=7.6, 6.5, 2.1 Hz), 6.21 (1 H, m), 6.08 (1 H, ddd, J=10.2, 3.8, 2.0 Hz), 5.58 (1 H, m), 4.83 (1 H, m), 2.86 (1 H, dd, J=17.0, 8.4 Hz), 2.77 (1 H, m), 2.50 (1 H, dd, J=17.0, 2.6 Hz), 2.24 (1 H, m), 1.72 (1 H, ddd, J=13.0, 11.6, 9 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ 175.4, 165.1, 133.8, 133.5, 132.8, 131.3, 131.2, 129.7, 126.7, 125.5, 74.0, 68.4, 35.8, 31.6, 29.2

Lactone **8**. Method B, 6 equiv. of LiOAc, was used with the same work-up as in Method A except that EtOAc was used to extract the product. Compound **3** (69 mg, 0.50 mmol) gave **7** (50 mg, 0.26 mmol, 51% yield, >95% *cis*) after flash chromatography using pentane–Et_2O 2:8 as the eluent. The spectral data were in accordance with those earlier reported in the literature.[8c]

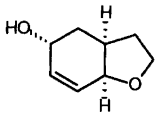
Assignment of the stereochemistry of **4b**. 25 mg (90 μmol) of **4b** were stirred in 5 ml 5% KOH in MeOH–H_2O 9:1 at 40 °C for 3 h. The solvent was evaporated and the residual crude mixture was purified by flash chromatography using pentane–Et_2O (1:1) as the eluent to give 10 mg of the alcohol **11** (79%).

Assignment of the stereochemistry of **4d**. The assignment of **4d** was carried out in analogy with that of **4b** to give the alcohol **11** as the major stereoisomer.

Assignment of the stereochemistry of **4e**. The assignment of **4e** was carried out in analogy with that of **4b** to give the alcohol **10** as the major stereoisomer.

Assignment of the stereochemistry of lactone **7**. 35 mg (120 μmol) of **7** were stirred in 5 ml 5% KOH in MeOH–H_2O 9:1 at 40 °C for 2 h. The reaction mixture was then acidified using HCl (conc.) and stirred for 1 h. The solvent was evaporated off and the residual crude mixture was purified by flash chromatography using EtOAc as the eluent to give 15 mg (97 μmol) of alcohol **12** (81%).

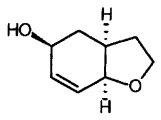
trans *Alcohol* **10**. 24 mg (132 μmol) of **4a** were stirred in 3 ml of 5% KOH in MeOH–H_2O 9:1 at 40 °C for 2 h. The solvent was evaporated off and the residual crude mixture was purified by flash chromatography using pentane–Et_2O (1:1) as the eluent to give 15 mg (108 μmol, 82%) of the *trans* alcohol **10**.



10

R_f(pentane–ether 50:50) 0.14. ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.99 (1 H, m), 5.88 (1 H, ddd, J=10.1, 3.7, 1.2 Hz), 4.25 (1 H, br), 4.22 (1 H, m), 3.91 (1 H, m), 3.76 (1 H, app dt, J=8.2, 6.7 Hz), 2.58 (1 H, m), 2.10 (1 H, m), 1.88 (1 H, ddd, J=13.3, 8.8, 4.6 Hz), 1.78–1.63 (2 H, m), 1.58 (1 H, br). ^{13}C NMR (100 MHz; $CDCl_3$): δ 132.3, 129.0, 73.9, 66.8, 63.5, 33.5, 33.3, 30.7.

cis *Alcohol* **11**. The reaction was performed as described for **10** using **4b** to give the *cis*-alcohol **11**.

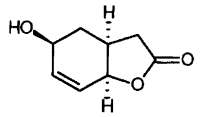


11

R_f(pentane–ether 50:50) 0.14. ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.94 (1 H, m), 5.88 (1 H, ddd, J=9.8, 3.5, 2.0 Hz), 4.10 (1 H, br), 4.01 (2 H, m), 3.79 (1 H, app dt, J=8.7, 5.5 Hz), 2.33 (1 H, m), 2.19 (1 H, m), 1.93 (1 H, m), 1.70 (1 H, m), 1.62 (1 H, br), 1.32 (1 H, app dt, J= 12.4, 10.4 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ 136.3, 126.0, 73.8, 67.4, 67.1, 35.10, 35.08, 32.6.

Assignment of the stereochemistry of alcohol **11**. **11** (10 mg, 71 μmol), was dissolved in 2 ml CH_2Cl_2 containing 14 μl (107 μmol, 1.5 equiv.) NEt_3. To this solution was added 7 μl (107 μmol, 1.5 equiv.) AcCl and the reaction mixture was stirred for 2 h. The solvent was evaporated off and the crude product was purified by flash chromatography using pentane: Et_2O 75:25 as the eluent to give **4c** (10 mg, 55 μmol, 77%) with NMR data in accordance with those reported in the literature.[8b]

Lactone alcohol **12**. 35 mg (120 μmol) of **8** were stirred in 5 ml 5% KOH in MeOH–H_2O 9:1 at 40 °C for 2 h. The reaction mixture was then acidified using HCl (conc.) and stirred for 1 h. The solvent was evaporated off and the residual crude mixture was purified by flash chromatography using EtOAc as the eluent to give 15 mg (97 μmol, 81%) of the alcohol **12**.



12

R_f(EtOAc) 0.42. ^{1}H NMR (400 MHz; $CDCl_3$): δ 6.14 (1 H, m), 5.95 (1 H, m), 4.73 (1 H, m), 4.26 (1 H, m), 2.85 (1 H, ddd, J=17.5, 8.2, 0.5 Hz), 2.60 (1 H, m), 2.42 (1 H, dd, J=17.4, 1.8 Hz), 2.05 (1 H, m), 1.40 (1 H, m). ^{13}C NMR (100 MHz; $CDCl_3$): δ 175.8, 138.7, 123.2, 74.4, 65.6, 36.5, 33.5, 32.0.

References and notes

1. Bäckvall, J. E. 'Palladium-Catalyzed Oxidation of Dienes', in: Patai, S. and Rappoport, Z., Eds., *The Chemistry of Functional Groups: Polyenes and Dienes*, Wiley. *In press.*
2. Andersson, P. G. and Bäckvall, J. E. In: Pearson, W. H., Ed., *Advances in Heterocyclic Natural Product Synthesis*, Vol 3, JAI Press, Greenwich 1996, pp. 179–216.
3. (a) Heumann, A., Jens, K. J. and Réglier, M. 'Palladium Complex Catalyzed Oxidation Reactions', in: Karlin, K. D., Ed., *Progress in Inorganic Chemistry*, Vol. 42, Wiley, New York 1994, pp. 483–576; (b) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis'*, Wiley, Chichester 1995.
4. (a) Bäckvall, J. E., Hopkins, R. B., Grennberg, H., Mader, M. and Awasthi, A. K. *J. Am. Chem. Soc. 112* (1990) 5160; (b) Grennberg, H., Gogoll, A. and Bäckvall, J. E. *J. Org. Chem. 56* (1991) 5808; (c) Grennberg, H., Fazon, S. and Bäckvall, J. E. *Angew. Chem., Int. Ed. Engl. 32* (1993) 263; (d) Grennberg, H., Bergstad, K. and Bäckvall, J. E. *J. Mol. Catal. In press.*
5. (a) van Benthem, R. A. T. M., Hiemstra, H. and Speckamp, W. N. *J. Org. Chem. 57* (1992) 6083; (b) van Benthem, R. A. T. M., Hiemstra, H., Michels, J. J. and Speckamp, W. N. *J. Chem. Soc., Chem. Commun.* (1994) 357; (c) van Benthem, R. A. T. M., Hiemstra, H., van Leeuwen, P. W. N. M., Geus, J. W. and Speckamp, W. N. J. *Angew. Chem., Int. Ed. Engl. 34* (1995) 457.
6. (a) Larock, R. C. and Hightower, T. R. *J. Org. Chem. 58* (1993) 5298; (b) Larock, R. C. and Hightower, T. R. *J. Org. Chem. 61* (1996) 3584.
7. Rönn, M., Bäckvall, J. E. and Andersson, P. G. *Tetrahedron Lett. 36* (1995) 7749.
8. (a) Bäckvall, J. E. 'Stereocontrol in Palladium-Catalyzed Reactions', in: Bateson, J. H. and Mitchell, M. B., Eds., *Organometallic Reagents in Organic Synthesis*, Academic Press, London 1994, pp. 81–97; (b) Bäckvall, J. E. and Andersson, P. G. *J. Am. Chem. Soc. 114* (1992) 6374; (c) Bäckvall, J. E., Granberg, K. L., Andersson, P. G., Gatti, R. and Gogoll, A. *J. Org. Chem. 58* (1993) 5445.
9. Bäckvall, J. E. and Andersson, P. G. *J. Am. Chem. Soc. 112* (1990) 3683.
10. Bäckvall, J. E., Andersson, P. G. and Vágberg, J. O. *Tetrahedron Lett. 30* (1989) 137.
11. (a) Tsuji, J., Yamakawa, T., Kaito, M. and Mandai, T. *Tetrahedron Lett. 19* (1978) 2075; (b) Trost, B. M., Verhoeven, T. R. and Fortunak, J. M. *Tetrahedron Lett. 20* (1979) 2301; (c) Andersson, P. G. and Schab, S. *Organometallics 14* (1995) 1.
12. Bäckvall, J. E. *Ligand Control in Some Selective Palladium-Catalyzed Reactions*, Abstract from the Third Conference on Catalysis, the Taniguchi Foundation, Sanda, Hyogo, Japan, 1984, pp. 35–40.
13. When a carbon nucleophile was used in place of an oxygen nucleophile, the diene corresponding to **9** was isolated. In this case the diene is more stable due to the lower leaving-group ability of the carbon: Rönn, M. *Unpublished results.*
14. For nucleophilic attack on (π-allyl)palladium complexes in DMSO see Tsuji, J., Takahashi, H. and Morikawa, N. *Tetrahedron Lett.* (1965) 4387. For nucleophilic attack on (π-allyl)palladium complexes with 1,4-benzoquinone as ligand see Bäckvall, J. E., Nordberg, R. E. and Wilhelm, D. *J. Am. Chem. Soc. 107* (1985) 6892; Bäckvall, J. E. and Gogoll, A. *Tetrahedron Lett. 29* (1988) 2243.
15. Colloidal palladium has been isolated, characterized and used in oxidation reactions.[15a,b] (a) Vargaftik, M. N., Zagorodnikov, V. P., Stolarov, I. P., Moiseev, I. I., Kochubey, D. I., Likholobov, V. A., Chuvilin, A. L. and Zamarev, K. I. *J. Mol. Catal. 53* (1989) 315; (b) Moiseev, I. I., Stromnova, T. A. and Vargaftik, M. N. *J. Mol. Catal. 86* (1994) 71.
16. Recently palladium clusters stabilized by propylene carbonate was reported: Reetz, M. T. and Lohmer, G. *J. Chem. Soc., Chem. Commun.* (1996) 1921.
17. (a) Wayland, B. B. and Schramm, R. F. *Inorg. Chem. 8* (1969) 971; (b) Davies, J. A. and Hartley, F. R. *Chem. Rev. 81* (1981) 79.
18. Bäckvall, J. E., Andersson, P. G., Stone, G. B. and Gogoll, A. *J. Org. Chem. 56* (1991) 2988.

Received October 11, 1996.