Improved Palladium-Catalyzed 1,4-Haloacyloxylation and 1,4-Diacyloxylation of Cyclic Conjugated Dienes

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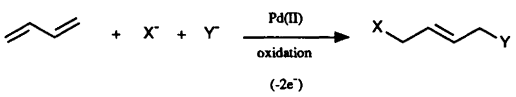
Improved procedures for the palladium-catalyzed 1,4-oxidation of cyclic conjugated dienes have been developed. In the new procedures the reactions are performed in acetone or ethyl acetate in the presence of the appropriate carboxylic acid. Thus, palladium-catalyzed oxidations of cyclic conjugated dienes in acetone in the presence of a carboxylic acid and lithium chloride using *p*-benzoquinone as the oxidant leads to an efficient *cis*-1,4-chloroacyloxylation. If the reaction is performed in the absence of lithium chloride, but under otherwise identical conditions, a 1,4-diacyloxylation of the conjugated diene takes place. 1,4-Bromoacyloxylation occurs if lithium bromide is used in place of lithium chloride in the palladium-catalyzed oxidation. These new procedures allow the use of a variety of carboxylates in Pd-catalyzed haloacyloxylations and diacyloxylations.

We have recently reported procedures for the palladium-catalyzed 1,4-functionalizations of conjugated dienes.[1-4] In these reactions two nucleophiles (X^-, Y^-) are introduced in the 1- and 4-positions of the diene [eqn. (1)]. In all cases so



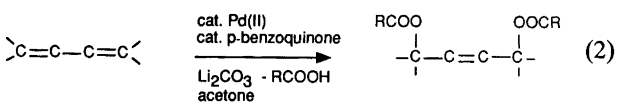
(1)

far, at least one of the nucleophiles added came from the solvent. Thus, in the 1,4-chloroacetoxylation ($X^- = OAc^-$, $Y^- = Cl^-$) or 1,4-diacetoxylation ($X^- = Y^- = OAc^-$) acetic acid served as the solvent. We now report improved procedures for the 1,4-haloacyloxylation and 1,4-diacyloxylation in a non-nucleophilic organic solvent which allows the use of a variety of carboxylates as nucleophiles.

Results and discussion

In the palladium-catalyzed 1,4-diacetoxylation the stereochemistry can be controlled to give either *cis* or *trans* 1,4-addition. This is explained by the formation of an intermediate *trans*-4-acetoxy-(π-allyl)palladium complex in which the acetate can be directed towards either *cis* or *trans* attack.[2a,5] It would be of great synthetic interest to extend this procedure to other carboxylates which may have better leaving-group properties and/or higher stability towards basic hydrolysis. Carboxylates without α-protons such as pivalate and benzoate are also of interest. One practical limitation to the original procedure is that the carboxylic acid serves as the solvent. However, we have now found that the use of acetone or ethyl acetate as the solvent in the presence of 5–10 equiv. of the appropriate carboxylic acid results in an efficient diacyloxylation reaction. This also leads to simpler work-up procedures.

Reaction of the appropriate conjugated diene with the carboxylic acid in acetone in the presence of Li_2CO_3, *p*-benzoquinone and a catalytic amount of a Pd^{II} salt afforded the dicarboxylate in good yields [eqn. (2)].[6] Results from diacyloxylation of 1,3-cyclohexadiene and 1,3-cycloheptadiene are given in Table 1. Acetone was found to be a good



(2)

solvent for this reaction. The reations also worked satisfactorily, but slowly, in tetrahydrofuran and ethyl acetate, whereas acetonitrile gave a poor yield. It is interesting to note that the acetone procedure gave a slightly higher *trans* selectivity in the diacetoxylation compared with the original procedure[2a] in acetic acid.

An efficient chloroacyloxylation was obtained when the appropriate diene was allowed to react with a carboxylic acid and lithium chloride in acetone in the presence of *p*-benzoquinone and catalytic amounts of a Pd^{II} salt. Several different carboxylic acids afforded a high yield of 1,4-chlorocarboxylate with 1,3-cyclohexadiene. Some results from the 1,4-chloroacyloxylations of 1,3-cyclohexadiene and 1,3-cycloheptadiene are given in Table 2. In all cases the chloroacyloxylations were highly stereoselective (>98 % *cis*). The 1,4-regioselectivity was >98 % for the

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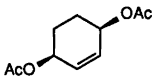
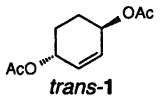
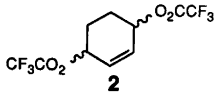
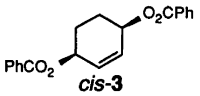
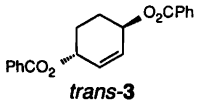
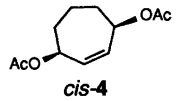
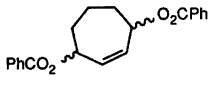
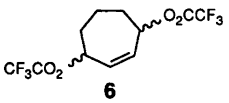
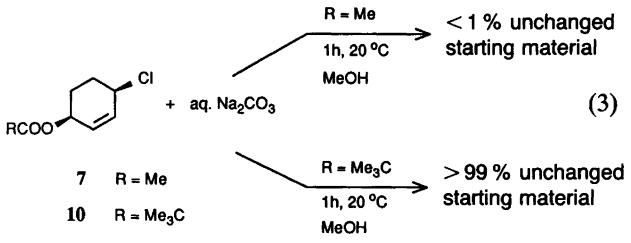
Table 1. Palladium-catalyzed 1,4-diacyloxylation of conjugated dienes in acetone.[a]

Diene	Carboxylic Acid	Method[b]	Product	Yield (%)[c]	*cis/trans*
	CH_3COOH	A	 *cis*-**1**	85	83/17
		C	 *trans*-**1**	87	7/93
	CF_3COOH	B	 **2**	94	23/77
	PhCOOH	A	 *cis*-**3**	85 65[d]	93/7 99/1
		B	 *trans*-**3**	97 70[d]	20/80 3/97
	CH_3COOH	B	 *cis*-**4**	100 80[d]	92/8 >99 % *cis*
	PhCOOH	A	 **5**	92	70/30
	CF_3COOH	A	 **6**	50	38/62

[a]The reaction was performed in acetone in the presence of 5–10 equiv. of the corresponding acid using 5 mol % of $Pd(OAc)_2$. The oxidant was either *p*-benzoquinone or catalytic *p*-benzoquinone–MnO_2. [b]Method A: no salt of the carboxylic acid was added; Method B: in the presence of the lithium salt of the carboxylic acid; Method C: As method B but with MnO_2–catalytic *p*-benzoquinone. [c]Isolated yields. [d]Purified by recrystallization or column chromatography.

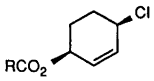
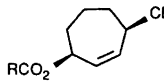
six-membered ring, but from the seven-membered ring it was in the range 87–93 %. The 1,2-isomer formed in small amounts for the seven-membered ring was shown by ^1H NMR to be of *cis* stereochemistry. The procedure works well with 1,3-cyclohexadiene and 1,3-cycloheptadiene, but fails for cyclopentadiene. Acyclic dienes gave poor yields with the acetone procedure. Thus, (*E,E*)- and (*E,Z*)-2,4-hexadiene afforded only 18 and 10 %, respectively, of the corresponding chloroacetates using the new procedure. This should be compared with the original chloroacetoxylation which gave 50–60 % yield with the same dienes.[3] The reason for the slow chloroacyloxylation of these acylic dienes in acetone is not obvious.

As mentioned above, pivalates are useful in cases where nucleophilic attack at the carbonyl has to be avoided or when strong bases are present. To demonstrate this point, the chlorocarboxylates **7** and **10** were treated with aqueous Na_2CO_3 in methanol [eqn. (3)]. The chloroacetate **7** was completely hydrolyzed after 1 h at ambient temperature according to GLC analysis.[7] On the other hand, the chloropivalate **10** was essentially unchanged (>99 %) after 1 h under the same reaction conditions.[8] Chlorobenzoates are also of synthetic interest since after substitution of the chloride, the benzoate may be substituted either classically (S_N2, S_N2') or via metal-catalysis.[9,10]



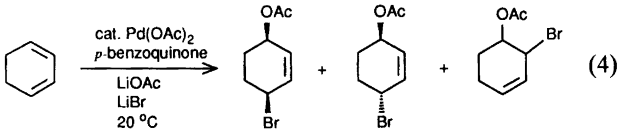
We have also extended the halocarboxylation reaction to include bromide as a nucleophile. When the bromoacetoxylation of 1,3-cyclohexadiene was performed in acetone, the stereoselectivity was poor, resulting in an almost 1:1 mixture of the *cis*- and *trans*-product. Attempts to replace acetone with acetonitrile, dimethyl sulfoxide or dioxane did

Table 2. Palladium-catalyzed 1,4-chloroacyloxylation of conjugated dienes in acetone.[a]

Diene	Carboxylic acid	Product	Yield (%)[b]
			
	MeCOOH	**7** R=Me	88
	$MeCH_2COOH$	**8** R=$MeCH_2$	82
	$Me_2CHCOOH$	**9** R=Me_2CH	87
	Me_3CCOOH	**10** R=Me_3C	87
	PhCOOH	**11** R=Ph	70
			
	MeCOOH	**12** R=Me	69[c]
	Me_3CCOOH	**13** R=Me_3C	56[c]
	PhCOOH	**14** R=Ph	60[c]

[a]The reaction was performed in acetone in the presence of 1.5–2 equiv. of LiCl, 0.5–2 equiv. of Li_2CO_3 and 5–10 equiv. of the corresponding acid using 5 mol % of the Pd^{II} catalyst. The oxidant was *p*-benzoquinone. [b]Isolated yields. [c]Contaminated with small amounts of the *cis*-1,2-isomer: for **12**, 1,4:1,2 = 90:10; for **13**, 1,4:1,2 = 87/13; for **14**, 1,4:1,2 = 93:7.

not improve the stereoselectivity. However, ethyl acetate as the solvent led to a significant improvement in selectivity and yield. The use of 4 equiv. of acetic acid (ethyl acetate–acetic acid = 14:1) gave a *cis*:*trans* ratio of 89:11 [eqn. (4)]. In contrast with the chloroacetoxylation, which is highly 1,4-selective, the bromoacetoxylation product was always contaminated with small amounts of the 1,2-isomer (1,4:1,2 ~ 90:10). An isomerization of *cis*-1,4-bromoacetate (*cis*-**15**) to the 1,2- and *trans*-1,4-isomer (**15'** and *trans*-**15**) to account for the latter products seems unlikely since the ratio between the three isomers *cis*-**15**, *trans*-**15** and **15'** was essentially unchanged during the reaction.



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EtOAc/HOAc	*cis*-**15**		*trans*-**15**		**15'**	Yield (%)
5/1[a]	69	:	23	:	8	70
5/1[b]	63	:	28	:	10	83
14/1[c]	83	:	10	:	8	65

[a]Acid:LiBr:diene = 8:1.5:1. [b]Acid:LiBr:diene = 10:1.5:1. [c]Acid:LiBr:diene = 4:1.3:1.

Conclusions

The introduction of carboxylates other than acetate in the 1,4-haloacyloxylation and 1,4-diacyloxylation of conjugated dienes extends the use of these oxidation products as building blocks. The improved procedures should be useful in the following respects. (a) Compounds that are stable towards hydrolysis and enolization are available. (b) The procedures provide better leaving groups in the classical S_N2 and S_N2' reactions as well as milder Pd(0)-catalyzed substitutions. (c) Asymetric synthesis utilizing readily available acids from the chiral pool could be realized. (d) Annulation reactions with nucleophiles incorporated into the carboxylic acid for the synthesis of lactones and other heterocycles would be possible.

Experimental

NMR spectra were obtained with a Varian XL 300 FT spectrometer, ^1H NMR at 299.3 MHz, and ^{13}C NMR at 75.4 MHz. Assignment of ^{13}C NMR spectra was achieved by running 2D NMR shift correlation experiments. The software was supplied by the manufacturer. Some ^{13}C–^1H shift correlation experiments were performed with a modified sequence developed recently by Reynolds *et al.*[11] Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane, Me_2Si, for ^1H spectra. For ^{13}C spectra the chemical shifts are reported relative to the central peak of internal $CDCl_3$ (77.00 ppm). Infrared spectra were recorded with a Perkin Elmer 1600 FT-IR spectrometer. Analytical GLC was performed on a Varian 3400 Gas Chromatograph using a 30-m DB5 capillary column. Chemical ionization (CI) spectra were recorded on a Finnigan INCOS 50 mass spectrometer connected to a Varian 3400 Gas Chromatograph, with methane as the ionizing gas. High-pressure liquid chromatography (HPLC) was performed using a Waters 501 HPLC pump with a Waters RCM 8×10 equipped with a Resolve silica column (10-μ packing, 0.8×10 cm) connected to a Waters differential refractometer and a Waters differential refractometer electronic unit. Bulb-to-bulb distillations were performed with a Büchi Kugelrohr apparatus. Melting points were obtained on a Büchi apparatus and are uncorrected. Elementary analyses were performed at *Engelskirschen Analytische Laboratorien*, West Germany.

Acetic acid (100 % p.a.), acetone (p.a.), and manganese (IV) oxide (active precipitated) were purchased from Merck. *p*-Benzoquinone (98 %), anhydrous lithium bromide (99 %), lithium chloride (99 %) and 1,3-cyclohexadiene (distilled before use) were purchased from Aldrich. 1,3-Cycloheptadiene was prepared according to a literature procedure.[12]

General procedure for palladium(II)-catalyzed 1,4-diacyloxylation of conjugated cyclic dienes. Method A. Unless otherwise noted, all reactions were performed at room temperature in acetone using $Pd(OAc)_2$ as the catalyst (0.05 equiv.). The amount of acid was 7–10 equiv. and the amount of *p*-benzoquinone was 2.1 equiv.

Method B. As above but with the lithium salt of the acid added.

Method C. As method B but with the use of catalytic amount of *p*-benzoquinone (0.25 equiv.) added together with manganese(IV) oxide (1.25 equiv.).

cis-*1,4-Diacetoxy-2-cyclohexene* (*cis*-**1**). Method A was used. To a stirred solution of $Pd(OAc)_2$ (90 mg, 0.40 mmol), acetic acid (4.80 g, 80.0 mmol) and *p*-benzoquinone (1.80 g, 16.8 mmol) in acetone (25 ml) was added 1,3-cyclohexadiene (640 mg, 8.00 mmol) via syringe over 2 h 15 min. After a total reaction time of 15 h, the acetone was removed *in vacuo* and the residue diluted with brine (25 ml) and extracted with ether/pentane (1×40 ml, 3×20 ml, 1:1). The combined organic layers were washed with 2 M NaOH (4×10 ml) whereupon the basic layers were back-extracted with ether–pentane (20 ml, 1:1). After drying ($MgSO_4$) and evaporation of the solvent, 1.40 g (88 %) of a yellow oil was collected which according to ^1H NMR spectroscopy was 96 % of a mixture of *cis*-**1** (83 %) and *trans*-**1** (17 %) and 4 % of the Diels–Alder adduct between 1,3-cyclohexadiene and *p*-benzoquinone. The NMR data were fully consistent with those previously reported.[2a]

Following the same procedure but using 1.25 equiv. MnO_2 and only 0.25 equiv. of *p*-benzoquinone (method C) gave 59 % yield of a mixture of *cis*-**1** (58 %) and *trans*-**1** (42 %).

trans-*1,4-Diacetoxy-2-cyclohexene* (*trans*-**1**). Method C was used. To a stirred mixture of $Pd(OAc)_2$ (16.8 mg, 0.075 mmol), $LiOAc \cdot 2H_2O$ (171 mg, 1.65 mmol), *p*-benzoquinone (46 mg, 0.043 mmol), MnO_2 (158 mg, 1.82 mmol), and acetic acid (0.50 ml, 8.3 mmol) in 2.5 ml acetone was added 1,3-cyclohexadiene (120 mg, 1.50 mmol) and pentadecane (50 µl, internal standard). Work-up was performed as for *cis*-**1** after 11 h at room temperature. GLC analysis indicated 92 % yield, HPLC and ^1H NMR analyses indicated a *trans*:*cis* ratio of 93:7. Chromatography on silica (hexane, hexane–ether = 85:15) afforded 260 mg (87 %) of *trans*-**1**. The ^1H NMR spectrum was consistent with that previously reported.[2a]

1,4-Bis(trifluoroacetoxy)-2-cyclohexene (**2**). Following method B, 1,3-cyclohexadiene (640 mg, 8.00 mmol) was added over 2.5 h to a solution of $Pd(OAc)_2$ (90 mg, 0.40 mmol), trifluoroacetic acid (9.50 g, 83.3 mmol), lithium trifluoroacetate (202 mg, 0.170 mmol) and *p*-benzoquinone (1.82 g, 16.8 mmol) in acetone (24 ml). After the reaction had been stirred for 23 h, the acetone was removed *in vacuo* and the residue was extracted thoroughly with pentane–ether (total 125 ml, 1:1). The organic phase was washed with satd. Na_2CO_3 (4×30 ml) and dried ($MgSO_4$). Concentration *in vacuo* afforded an oil, 2.31 g (94 %), which solidified slowly. According to ^1H NMR and GLC it consisted of *trans*-**2** and *cis*-**2** in a ratio of 77:23 contaminated with a small amount of monoalcohol.[13] Further characterization was obtained through the mild hydrolysis of the stereoisomeric mixture to the known diols.[2a]

trans-**2**: m.p. 37.0–38.5 °C; ^1H NMR ($CDCl_3$): δ 6.12 (br d, 2 H, CH=CH), 5.51 (m, 2 H, CHO_2CCF_3), 2.31–2.20 (m, 2 H, CH_e-CH_e), 1.99–1.89 (m, 2 H, CH_a-CH_a); ^{13}C NMR ($CDCl_3$) δ 156.97 (q, *J* 42 Hz, O_2CCF_3), 129.58 (CH=CH), 114.46 (q, *J* 286 Hz, CF_3), 70.98 (CHO_2CCF_3), 24.19 [$(CH_2)_2$]. IR (neat): 1780, 1377, 1226, 1149 (br), 1006, 911, 777 cm^{-1}. MS(CI−CH_4): *m/z* (rel. intensity) 194 (9), 193 (100), 192 (2), 151 (1), 115 (5), 107 (2).

cis-**2**: ^1H NMR ($CDCl_3$): δ 6.08 (br s, 2 H, CH=CH), 5.45 (m, 2 H, CHO_2CCF_3), 2.09 [m, 2 H $(CH_2)_2$]; ^{13}C NMR ($CDCl_3$): δ 156.97 (q, *J* 42 Hz, O_2CCF_3), 129.70 (CH=CH), 114.46 (q, *J* 285 Hz, CF_3), 71.29 (CHO_2CCF_3), 23.94 [$(CH_2)_2$]. MS(CI−CH_4): *m/z* (rel. intensity) 194 (9), 193 (100), 192 (3), 115 (2), 111 (4).

cis-*1,4-Dibenzoyloxy-2-cyclohexene* (*cis*-**3**). Method A was used. To a stirred mixture of $Pd(OAc)_2$ (46 mg, 0.20 mmol), benzoic acid (3.71 g, 30.4 mmol), and *p*-benzoquinone (950 mg, 8.80 mmol) in acetone (25 ml) was added 1,3-cyclohexadiene (320 mg, 4.00 mmol) via syringe over 4 h. After 17 h at room temperature, the acetone was removed *in vacuo*, followed by addition of ether (75 ml) to the residue. The ether phase was washed with 2 M NaOH (2×20 ml)[14] and finally once with 2 M NaOH (10 ml) with some $NaBH_4$ added. The combined basic layers were back-extracted with ether (2×10 ml) whereupon the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent afforded 1.10 g (85 %) of an oil which slowly solidified. The ^1H NMR and GLC showed 93 % *cis*-**3** and 7 % *trans*-**3**. Recrystallization from hexane afforded pure (>99 %) *cis*-**3** in 65 % yield, m.p. 79.5–82.5 °C. Further characterization was obtained by hydrolysis to the known diol:[2a] ^1H NMR ($CDCl_3$): δ 8.09 (m, 2 H, *ortho*), 7.56 (m, 1 H, *para*), 7.44 (m, 2 H, *meta*), 6.10 (br d, *J* 1.5 Hz, 2 H, olefinic), 5.54 (m, 2 H, CHO_2CPh), 2.10 [m, 4 H, $(CH_2)_2$]. ^{13}C NMR ($CDCl_3$): δ 165.98 (O_2CPh), 132.96 (*para*), 130.46 (olefinic), 130.20 (*ipso*), 129.60 (*ortho*), 128.29 (*meta*), 67.82 (CHO_2CPh), 25.05 [$(CH_2)_2$]. IR (KBr): 1709 (br), 1342, 1316, 1265, 1121, 1108, 1012, 710 cm^{-1}. MS (CI−CH_4): *m/z* (rel. intensity) 229 (2), 202 (15), 201 (100), 200 (3), 151 (4), 123 (22), 106 (2), 105 (33), 81 (2), 79 (7); Found: C, 74.44; H, 5.54. Calc. for $C_{20}H_{18}O_4$: C, 74.50; H, 5.63.

trans-*1,4-Dibenzoyloxy-2-cyclohexene* (*trans*-**3**). Method B was used. 1,3-Cyclohexadiene (640 mg, 8.00 mmol) was added to a mixture of $Pd(OAc)_2$ (90 mg, 0.40 mmol), benzoic acid (9.20 g, 75.4 mmol), lithium benzoate (0.90 g, 7.0 mmol), and *p*-benzoquinone (1.82, 16.8 mmol) in acetone (25 ml) at 32 °C over 4 h. After 14 h, a work-up as for *cis*-**3** yielded 2.50 g (97 %) of a pale yellow solid which according to ^1H NMR spectroscopy was *trans*-**3** (80 %) and *cis*-**3** (20 %). Flash chromatography on silica (hexane–ethyl acetate 95:5) afforded 1.80 g (70 %) of *trans*-**3** as a colorless solid (contaminated with 3 % of *cis*-**3**), m.p. 95.5–98.0 °C. Further characterization was obtained by hydrolysis to the known diol:[2a] HPLC: $k' = 2.0$ (hexane–ethyl acetate 90:10);

^{1}H NMR ($CDCl_3$): δ 8.06 (m, 2 H, *ortho*), 7.56 (m, 1 H, *para*), 7.44 (m, 2 H, *meta*), 6.09 (br d, *J* 1.2 Hz, 2 H, olefinic), 5.63 (br s, 2 H, CHO_2CPh), 2.38–2.29 (m, 2 H, CH_e-CH_e), 2.00–1.89 (m, 2 H, CH_a-CH_a). ^{13}C NMR ($CDCl_3$): δ 165.96 (O_2CPh), 132.94 (*para*), 130.42 (olefinic), 130.15 (*ipso*), 129.54 (*ortho*), 128.28 (*meta*), 68.00 (CHO_2CPh), 25.83 [$(CH_2)_2$]. IR (KBr): 2948, 1705, 1452, 1334, 1266, 1108, 1068, 936, 706 cm^{-1}.

cis-*1,4-Diacetoxy-2-cycloheptene* (*cis*-**4**). Method B was used. $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), acetic acid (1.20 g, 20.0 mmol), $LiOAc \cdot 2H_2O$ (816 mg, 8.00 mmol), *p*-benzoquinone (454 mg, 4.20 mmol) and 1,3-cycloheptadiene (188 mg, 2.00 mmol) in acetone (6.0 ml) was heated to 40 °C for 24 h. Work-up as for *cis*-**1** afforded 430 mg (100 %) of a solid, which according to ^{1}H NMR spectroscopy was 92 % *cis*-**4** and 8 % *trans*-**4**. Recrystallization from hexane yielded 340 mg (80 %) of isomerically pure *cis*-**4** (>99 % *cis*). The ^{1}H NMR data were fully consistent with those previously reported.[2a]

1,4-Dibenzoyloxy-2-cycloheptene (**5**). Method A was used. $Pd(OAc)_2$ (45 mg, 0.20 mmol), benzoic acid (4.88 g, 40.0 mmol), *p*-benzoquinone (908 mg, 8.40 mmol), and 1,3-cycloheptadiene (380 mg, 4.00 mmol) in acetone (12 ml) were stirred for 183 h at room temperature. Work-up as for *cis*-**3** afforded 1.24 g (92 %) of an almost pure (>96 %) oil which according to ^{1}H NMR was a mixture of *cis*-**5** and *trans*-**5** (ratio 7:3). The isomers were separated by flash chromatography (hexane–ethyl actate 95:5) on silica. Further characterization was obtained by hydrolysis to the diols. Samples of *cis*- and *trans*-2-cycloheptene-1,4-diols were obtained by hydrolysis of the known corresponding diacetates.[2a]

cis-**5**: m.p. 89.5–91.0 °C; ^{1}H NMR ($CDCl_3$): δ 8.07 (m, 2 H, *ortho*), 7.57 (m, 1 H, *para*), 7.45 (m, 2 H, *meta*), 5.90 (br s, 2 H, olefinic), 5.69 (br d, *J* 10.1 Hz, 2 H, CHO_2CPh), 2.13–1.76 [m, 6 H, $(CH_2)_3$]. ^{13}C NMR ($CDCl_3$): δ 165.64 (O_2CPh), 132.98 (*para*), 132.69 (olefinic), 130.30 (*ipso*), 129.61 (*ortho*), 128.33 (*meta*), 74.09 (CHO_2CPh), 32.50 [$(CH_2)_2CH_2$], 22.75 [$CH_2(CH_2)_2$]. IR (KBr): 2925, 1718, 1704, 1330, 1274, 1108, 712 cm^{-1}. MS (CI–CH_4): *m/z* (rel. intensity) 243 (2), 216 (16), 215 (100), 214 (2), 151 (2), 123 (9), 106 (4), 105 (55), 95 (3), 93 (8).

trans-**5**: m.p. 78.5–81.5 %. ^{1}H NMR ($CDCl_3$): δ 8.07 (m, 2 H, *ortho*), 7.57 (m, 1 H, *para*), 7.45 (m, 2 H, *meta*), 6.00 (br d, *J* 2.0 Hz, 2 H, olefinic), 5.74 (m, 2 H, CHO_2CPh), 2.04 [br s, 6 H, $(CH_2)_3$]. ^{13}C NMR ($CDCl_3$): δ 165.69 (O_2CPh), 133.21 (olefinic), 132.96 (*para*), 130.31 (*ipso*), 129.59 (*ortho*), 128.36 (*meta*), 72.16 (CHO_2CPh), 31.96 [$(CH_2)_2CH_2$], 20.14 [$CH_2(CH_2)_2$]. IR (neat): 1705, 1335, 1266, 1108, 1068, 1024, 937, 709 cm^{-1}. MS (CI–CH_4): *m/z* (rel. intensity) 216 (16), 215 (100), 151 (5), 123 (13), 106 (7), 105 (92), 95 (5), 93 (13).

By using 8 equiv. of benzoic acid and 4 equiv. of lithium benzoate in refluxing acetone (method A), a mixture enriched in *trans*-**5** product (55 % *trans*) was obtained in a quantitative yield.

1,4-Bis(trifluoroacetoxy)-2-cycloheptene (**6**). Method A was used. $Pd(OAc)_2$ (46 mg, 0.20 mmol), trifluoroacetic acid (4.56 g, 40.0 mmol), *p*-benzoquinone (908 mg, 8.40 mmol) and 1,3-cycloheptadiene (380 mg, 4.00 mmol) in acetone (12 ml). After 70 h at room temperature, a work-up as for **2** gave 638 mg (50 %) of an oil which according to NMR spectroscopy was *trans*-**6** (62 %) and *cis*-**6** (38 %) contaminated with small amounts of the monoalcohol.[13] Further characterization was obtained by means of mild hydrolysis to the diols. Samples of *cis*- and *trans*-2-cycloheptene-1,4-diols were obtained by hydrolysis of the known corresponding diacetates.[2a]

cis-**6**: ^{1}H NMR ($CDCl_3$): δ 5.96 (br d, 2 H, olefinic), 5.60 (m, 2 H, CHO_2CCF_3), 1.99 (br s, 6 H, $(CH_2)_3$]. MS (CI–CH_4): *m/z* (rel. intensity) 208 (6), 207 (55), 151 (2), 95 (2), 94 (9), 93 (100).

trans-**6**: ^{1}H NMR ($CDCl_3$): δ 5.84 (br s, 2 H, olefinic), 5.55 (m, CHO_2CCF_3), 2.17–1.83 [m, 6 H, $(CH_2)_3$]. MS (CI–CH_4): *m/z* (rel. intensity) 208 (7), 207 (58), 206 (3), 95 (2), 94 (7), 93 (100).

General procedure for palladium(II)-catalyzed 1,4-chloroacyloxylation of conjugated cyclic dienes. The reactions were performed at ambient temperature in acetone (3 ml mmol^{-1} diene) with 1.5–2 equiv. of LiCl and 0.5–2 equiv. of Li_2CO_3 (or the lithium carboxylate of the acid) using $PdCl_2$, Li_2PdCl_4 of $Pd(OAc)_2$ as the catalyst (0.05 equiv.). The amount of acid used was 5–10 equiv. *p*-Benzoquinone (2.1 equiv.) was used as the oxidant unless otherwise noted. Addition of 1,3-cyclohexadiene was performed via syringe over 2–4 h, while 1,3-cycloheptadiene was added in one portion.

cis-*1-Acetoxy-4-chloro-2-cyclohexene* (**7**). 1,3-Cyclohexadiene (641 mg, 8.0 mmol) was added over 2 h via syringe to a solution of $Pd(OAc)_2$ (90 mg, 0.40 mmol), LiCl (509 mg, 12.0 mmol), acetic acid (4.80 g, 80.0 mmol), and *p*-benzoquinone (1.82 g, 16.8 mmol) in acetone (24 ml) with added Li_2CO_3 (296 mg, 4.00 mmol). After 18 h at room temperature, a work-up as for *cis*-**1** afforded a pale yellow oil (1.25 g, 89 %) which according to ^{1}H NMR spectroscopy was a >97 % pure product contaminated with small amounts of Diels–Alder adduct. The ^{1}H NMR spectrum was consistent with that previously reported.[3]

cis-*1-Chloro-4-propionyloxy-2-cyclohexene* (**8**) was prepared by adding 1,3-cyclohexadiene (115 mg directly, 505 mg in 3.7 ml acetone over 2.5 h, total 7.70 mmol) to a mixture of $Pd(OAc)_2$ (87 mg, 0.39 mmol), LiCl (650 mg, 15.0 mmol), *p*-benzoquinone (1.76 g, 16.0 mmol), propionic acid (5.70 g, 77.0 mmol) and Li_2CO_3 (1.11 g, 15.0 mmol) in acetone (15 ml). The mixture was stirred for 10 h at room temperature and worked up as *cis*-**1** to yield 1.19 g

(82 %) of pure product: ^{1}H NMR ($CDCl_3$): δ 5.97 (dddt, *J* 10.0, 3.8, 1.7, 0.6 Hz, 1 H, CH=C*H*CHCl), 5.79 (dddt, *J* 10.0, 2.9, 1.1, 0.6 Hz, 1 H, CH=C*H*CHO$_2$CCH$_5$), 5.29 (m, 1 H, C*H*O$_2$CC$_2$H$_5$), 4.56 (m, 1 H, CHCl), 2.35 (q, *J* 7.6 Hz, 2 H, C*H*$_2$CH$_3$), 2.13 (m, 2 H, C*H*$_2$CHCl), 1.96 (m, 2 H, C*H*$_2$CHO$_2$CC$_2$H$_5$), 1.15 (t, *J* 7.6 Hz, 3 H, C*H*$_3$CH$_2$). ^{13}C NMR ($CDCl_3$): δ 173.99 (O$_2$*C*C$_2$H$_5$), 131.54 (CH=*C*HCHCl), 129.44 (CH=*C*HO$_2$CC$_2$H$_5$), 67.45 (*C*HO$_2$CC$_2$H$_5$), 53.54 (CHCl), 29.52 (CH$_2$CHCl), 27.68 (*C*H$_2$CH$_3$), 24.42 (*C*H$_2$CHO$_2$CC$_2$H$_5$), 9.05 (*C*H$_3$CH$_2$). IR (neat): 1737, 1366, 1227, 1183, 1082, 1024, 889, 768 cm^{-1}. MS (CI−CH$_4$): *m/z* (rel. intensity) 189 [(*M*+1)$^+$, 11], 153 (81), 123 (12), 117 (14), 115 (44), 95 (100), 86 (41), 84 (64), 79 (61), 75 (73); Found: C, 57.19; H, 6.92. Calcd. for $C_9H_{13}ClO_2$: C, 57.29; H, 6.99.

cis-*1-Chloro-4-isobutyryloxy-2-cyclohexene* (**9**). Performed as above with 10 equiv. of isobutyric acid. The reaction mixture was stirred for 12 h at room temperature. Work-up as for *cis*-**1** yielded a colorless oil which according to NMR was a pure product, 1.36 g (87 %): ^{1}H NMR ($CDCl_3$): δ 5.87 (dddt, *J* 10.0, 3.8, 1.7, 0.5 Hz, 1 H, CH=C*H*CHCl), 5.69 [dddt, *J* 10.0, 2.9, 1.0, 0.5 Hz, 1 H, CH=C*H*CHO$_2$CCH(CH$_3$)$_2$], 5.17 [m, 1 H, C*H*O$_2$CCH(CH$_3$)$_2$], 4.46 (m, 1 H, CHCl), 2.45 [sept., *J* 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.06–1.99 (m, 2 H, C*H*$_2$CHCl), 1.89–1.81 [m, 2 H, C*H*$_2$CHO$_2$CCH(CH$_3$)$_2$], 1.073 [d, *J* 7.0 Hz, CH(C*H*$_3$)$_2$ one of two diastereotopic], 1.073 [d, *J* 7.0 Hz, CH(C*H*$_3$)$_2$ one of two diastereotopic]. ^{13}C NMR ($CDCl_3$): δ 176.42 O$_2$*C*CH(CH$_3$)$_2$], 131.40 (CH=*C*HCHCl), 129.40 [CH=*C*HCHO$_2$CCH(CH$_3$)$_2$], 67.17 [*C*HO$_2$CCH(CH$_3$)$_2$], 53.44 (CHCl), 33.87 [*C*H(CH$_3$)$_2$], 29.45 (*C*H$_2$CHCl), 24.29 [*C*H$_2$CHO$_2$CCH(CH$_3$)$_2$], 18.82 [CH(*C*H$_3$)$_2$ one of two diastereotopic], 18.75 [CH(*C*H$_3$)$_2$ one of two diastereotopic]. IR (neat): 2973, 1732, 1256, 1228, 1189, 1157, 1071, 1018 cm^{-1}; MS (CI−CH$_4$), *m/z* (rel. intensity) 203 [*M*+1, 5], 168 (12), 167 (100), 117 (20), 115 (35), 89 (73), 79 (53), 75 (13), 71 (34).

cis-*1-Chloro-4-pivaloyloxy-2-cyclohexene* (**10**). To a mixture of $PdCl_2$ (71 mg, 0.40 mmol), Li_2CO_3 (1.18 g, 16.0 mmol), pivalic acid (8.18 g, 80.0 mmol), LiCl (640 mg, 15.2 mmol), and *p*-benzoquinone (1.82 g, 16.8 mmol) in acetone (24 ml) was added 1,3-cyclohexadiene (641 mg, 8.00 mmol) over 2 h via syringe. After 25 h, work-up as for *cis*-**3** afforded 1.51 g (87 %) of a colorless oil of >98 % purity: ^{1}H NMR ($CDCl_3$): δ 5.96 (dddd, *J* 10.0, 3.8, 1.8, 0.8 Hz, 1 H, CH=C*H*CHCl), 5.78 [dddt, *J* 10.0, 2.9, 1.0, 0.7 Hz, 1 H, CH=C*H*CHO$_2$CC(CH$_3$)$_3$], 5.25 [m, 1 H, C*H*O$_2$CC(CH$_3$)$_3$], 4.57 (m, 1 H, CHCl), 2.17–2.09 (m, 2 H, C*H*$_2$CHCl), 1.98–1.90 [m, 2 H, C*H*$_2$CHO$_2$CC(CH$_3$)$_3$], 1.21 [s, 9 H, (CH$_3$)$_3$]. ^{13}C NMR ($CDCl_3$): δ 178.0 [O$_2$*C*C(CH$_3$)$_3$], 131.42 (CH=*C*HCHCl), 129.60 [CH=*C*HCHO$_2$CC(CH$_3$)$_3$], 67.32 [*C*HO$_2$CC(CH$_3$)$_3$], 53.66 (CHCl), 38.67 [*C*(CH$_3$)$_3$], 29.58 (*C*H$_2$CHCl), 27.06 [(CH$_3$)$_3$], 24.37 [*C*H$_2$CHO$_2$CC(CH$_3$)$_3$]. IR (neat): 2969, 1728, 1480, 1280, 1228, 1156, 1035, 1016 cm^{-1}. MS (CI−CH$_4$): *m/z* (rel. intensity) 217 [(*M*+1)$^+$, 2], 182 (13), 181 (100), 143 (4), 131 (10), 123 (4), 117 (8), 115 (26), 104 (5), 103 (90), 96 (3), 95 (27), 86 (9), 85 (21), 84 (12), 80 (3), 79 (40). Found: C, 60.83; H, 7.81. Calcd. for $C_{11}H_{17}ClO_2$: C, 60.97; H, 7.91.

cis-*1-Benzoyloxy-chloro-2-cyclohexene* (**11**). To a stirred solution of Li_2PdCl_4 (105 mg, 0.40 mmol), LiCl (509 mg, 12.0 mmol), lithium benzoate (549 mg, 4.30 mmol), benzoic acid (7.80 g, 63.9 mmol) and *p*-benzoquinone (1.82 g, 16.8 mmol) in acetone (30 ml), was added 1,3-cyclohexadiene (651 mg, 8.00 mmol) via syringe over 4 h. After an additional 14 h the reaction was worked up as *cis*-**3** to afford a yellow oil (1.50 g) of 94 % purity. The Diels–Alder adduct between 1,3-cyclohexadiene and *p*-benzoquinone, 6 % in the crude product, was easily removed by flash chromatography (hexane–ethyl acetate 90:10) on silica to yield 1.33 g (70 %) of pure product, HPLC: *k'* = 1.6 (hexane–ethyl acetate 90:10). ^{1}H NMR ($CDCl_3$): δ 8.05 (m, 2 H, *ortho*), 7.55 (m, 1 H, *para*), 7.43 (m, 2 H, *meta*), 6.01 (ddd, *J* 10.0, 3.7, 1.6 Hz, 1 H, CH=C*H*CHCl), 5.92 (ddt, *J* 10.0, 2.8, 0.8 Hz, 1 H, CH=C*H*CHO$_2$CPh), 5.53 (m, 1 H, C*H*O$_2$CPh), 4.58 (m, 1 H, CHCl), 2.21–2.04 [m, 4 H, (CH$_2$)$_2$]. ^{13}C NMR ($CDCl_3$): δ 165.83 (O$_2$*C*Ph), 132.90 (*para*), 131.74 (CH=*C*HCHCl), 129.98 (*ipso*), 129.49 (*ortho*), 129.22 (CH=*C*HCHO$_2$CPh), 128.20 (*meta*), 68.04 (*C*HO$_2$CPh), 53.47 (CHCl), 29.50 (*C*H$_2$CHO$_2$CPh), 24.49 (*C*H$_2$CHCl): IR (neat): 1716, 1452, 1315, 1270, 1109, 1070, 1026, 1014, 712 cm^{-1}; MS (CI−CH$_4$): *m/z* (rel. intensity) 237 [(*M*+1)$^+$, (22), 202 (15), 201 (100), 151 (19), 123 (79), 117 (23), 115 (61), 105 (84), 81 (11), 79 (96). Found: C, 65.78; H, 5.52. Calcd. for $C_{13}H_{13}ClO_2$: C, 65.96; H, 5.55.

cis-*1-Acetoxy-4-chloro-2-cycloheptene* (**12**) was prepared as for *cis*-**13** and worked up as for *cis*-**1**. Bulb-to-bulb distillation (75–85 °C/0.05 mmHg) afforded 648 mg (69 %) of a colorless oil which according to ^{1}H NMR spectroscopy was *cis*-**12** (90 %) and cis-*4-acetoxy-3-chloro-2-cycloheptene* (*cis*-**12'**) (10 %). The ^{1}H NMR spectrum of *cis*-**12** was completely consistent with data previously reported.[3] Compound *cis*-**12'** was isolated by preparative HPLC: *k'* = 2.1 (hexane–ethyl acetate 98:2). ^{1}H NMR ($CDCl_3$): δ 6.05 (ddd, *J* 11.1, 6.5, 5.5 Hz, 1 H, CH=CHCH$_2$), 5.82 (dddd, *J* 11.1, 7.4, 1.7, 1.0 Hz, 1 H, CH=C*H*CHCl), 5.10 (ddd, *J* 10.4, 4.0, 2.0 Hz, 1 H, C*H*OAc), 4.68 (dddt, *J* 7.4, 3.2, 2.0, 0.5 Hz, 1 H, CHCl), 2.37–2.12 [m, 1 H, C*H*$_2$(CH$_2$)$_2$ and 2 H, C*H*$_2$CH=CH], 2.09 (s, 3 H, CH$_3$CO$_2$), 2.01–1.77 (m, 2 H, C*H*CHCl), 1.67–1.55 [m, 1 H, C*H*$_2$(CH$_2$)$_2$]. MS (CI−CH$_4$): *m/z* (rel. intensity) 189 [(*M*+1)$^+$, 5], 154 (5), 153 (49), 131 (33), 130 (9), 129 (100), 111 (18), 93 (57), 88 (10), 86 (62), 84 (99).

cis-*1-Chloro-4-pivaloyloxy-2-cycloheptene* (**13**). 1,3-Cycloheptadiene (470 mg, 5.0 mmol) was added to a solution of Li_2PdCl_4 (65 mg, 0.25 mmol), LiCl (318 mg, 7.50 mmol), pivalic acid (5.11 g, 50.0 mmol), Li_2CO_3 (185 mg, 2.50 mmol), and *p*-benzoquinone (1.19 g, 11.0 mmol) in ace-

tone (15 ml). After 72 h of stirring at room temperature only 5–10 % of the diene remained. Work-up as for *cis*-**3** gave an oil which was bulb-to-bulb distilled (100 °C/0.05 mmHg) to yield 645 mg (56 %) of a solid which melts at RT, 87 % of *cis*-**13** and 13 % of *cis*-13-chloro-4-pivaloyloxy-2-cycloheptene (*cis*-**13'**).

cis-**13**: HPLC: $k' = 1.6$ (hexane–ethyl acetate 98:2). ^{1}H NMR ($CDCl_3$): δ 5.88 (dddd, *J* 12.0, 4.4, 2.3, 0.6 Hz, 1 H, CH=C*H*CHCl), 5.67 [dddd, *J* 12.0, 3.0, 1.7, 1.0 Hz, CH=C*H*CHO$_2$CC(CH$_3$)$_3$], 5.35 [m, 1 H, C*H*O$_2$CC(CH$_3$)$_3$], 4.65 (m, 1 H, CHCl), 2.21–1.71 [m, 6 H, (CH$_2$)$_3$], 1.21 [s, 9 H, (CH$_3$)$_3$]; ^{13}C NMR ($CDCl_3$): δ 177.65 [O$_2$*C*C(CH$_3$)$_3$], 133.85 [CH=*C*HCHO$_2$CC(CH$_3$)$_3$], 133.29 (CH=*C*HCHCl), 72.10 [*C*HO$_2$CC(CH$_3$)$_3$], 58.57 (CHCl), 36.03 (*C*H$_2$CHCl), 31.92 [*C*H$_2$CHO$_2$CC(CH$_3$)$_3$], 27.02 [(CH$_3$)$_3$], 22.60 [*C*H$_2$(CH$_2$)$_2$]. IR (neat): 2971, 2936, 1728, 1480, 1281, 1158, 1033, 992 cm^{-1}. MS (CI–CH$_4$): *m/z* (rel. intensity) 231 [(*M*+1)$^+$, 3], 196 (13), 195 (83), 143 (4), 131 (21), 130 (3), 129 (33), 111 (7), 104 (3), 103 (42), 95 (4), 94 (10), 93 (100), 86 (3), 85 (54).

cis-**13'** (in mixture with *cis*-**13**): ^{1}H NMR ($CDCl_3$): δ 6.04 (ddd, *J* 11.3, 6.5, 5.6 Hz, 1 H, CH=C*H*CH$_2$), 5.81 (dddd, *J* 11.3, 7.0, 1.7, 0.5 Hz, 1 H, CH=C*H*CHCl), 5.07 [ddd, *J* 9.9, 4.0, 2.0 Hz, 1 H, C*H*O$_2$CC(CH$_3$)$_3$], 4.66 (m, hidden, 1 H, C*H*Cl). ^{13}C NMR ($CDCl_3$): δ 137.44 (CH=*C*HCH$_2$), 127.26 (CH=*C*HCHCl), 73.29 [*C*HO$_2$CC(CH$_3$)$_3$], 60.79 (CHCl), 38.56 (*C*H$_2$CH=CH), 30.73 [*C*H$_2$CHO$_2$CC(CH$_3$)$_3$], 27.43 [(CH$_3$)$_3$], 23.16 [*C*HF$_2$(CH$_2$)$_2$]. MS (CI–CH$_4$): *m/z* (rel. intensity) 231 [(*M*+1)$^+$, 13], 196 (12), 195 (77), 131 (38), 130 (10), 129 (100), 111 (11), 103 (28), 93 (22), 85 (44), 75 (10).

cis-*1-Benzoyloxy-4-chloro-2-cycloheptene* (**14**). This was prepared as for *cis*-**13** but using a slightly larger volume of acetone (20 ml) and with lithium benzoate (961 mg, 1.50 mmol) in place of Li_2CO_3. Work-up as for *cis*-**3** and subsequent bulb-to-bulb distillation (190–200 °C/0.05 mmHg) afforded 749 mg (60 %) of a solid, which consisted of *cis*-**14** (93 %) and cis-*4-benzoyloxy-3-chloro-2-cycloheptene* (*cis*-**14'**) (7 %).

cis-**14**: ^{1}H NMR ($CDCl_3$): δ 8.06 (m, 2 H, *ortho*), 7.56 (m, 1 H, *para*), 7.44 (m, 2 H, *meta*), 5.94 (ddd, *J* 12.2, 6.4, 2.1 Hz, 1 H, CH=C*H*CHCl), 5.83 (dddd, *J* 12.2, 3.1, 1.4, 1.0 Hz, 1 H, C*H*=CHCHO$_2$CPh), 5.63 (m, 1 H, C*H*O$_2$CPh), 4.69 (m, 1 H, CHCl), 2.24–1.77 [m, 6 H, (CH$_2$)$_3$]. ^{13}C NMR ($CDCl_3$): δ 165.66 (O$_2$*C*Ph), 133.65 (CH=*C*HCHO$_2$CPh), 133.55 (CH=*C*HCHCl), 133.02 (*para*), 129.72 (*ipso*), 129.60 (*ortho*), 128.34 (*meta*), 73.00 (*C*HO$_2$CPh), 58.53 (CHCl), 36.06 (*C*H$_2$CHCl), 32.12 (*C*H$_2$CHO$_2$CPh), 22.64 [*C*H$_2$(CH$_2$)$_2$]. IR (neat): 1717, 1450, 1316, 1272, 1113, 1070, 1026, 712 cm^{-1}; MS (CI–CH$_4$): *m/z* (rel. intensity) 251 [(*M*+1)$^+$, 9], 216 (12), 215 (56), 153 (8), 151 (15), 131 (39), 130 (9), 129 (100), 123 (36), 105 (92), 95 (13), 93 (56). Found: C, 66.95; H, 6.03. Calcd. for $C_{14}H_{15}ClO_2$: C, 67.06; H, 6.04.

cis-*1-Acetoxy-4-bromo-2-cyclohexene* (**15**). A mixture of Pd(OAc)$_2$ (45 mg, 0.20 mmol), LiOAc · 2H$_2$O (0.82 g, 8.0 mmol), LiBr (0.11 g, 1.2 mmol), acetic acid (0.96 g, 16 mmol) and *p*-benzoquinone (0.90 g, 8.3 mmol) in ethyl acetate (12.0 ml) was stirred until all of the Pd(OAc)$_2$ dissolved. A solution of 1,3-cyclohexadiene (0.32 g, 4.0 mmol) in ethyl acetate (0.35 ml) and a solution of LiBr (0.35 g, 4.0 mmol) in ethyl acetate (1.0 ml) were added via syringe over 15 h. After a total reaction time of 27 h the ethyl acetate was removed *in vacuo*. Work-up as for *cis*-**1** yielded a pale yellow oil 570 mg (65 %) which consisted of *cis*-**15**, *trans*-**15**, and the 1,2-isomer **15'** in the ratio 83:10:8, contaminated with small amounts of the Diels–Alder adduct. The desired product was readily obtained by flash chromatography on silica (hexane–ethyl acetate 98:2).

cis-**15**: HPLC: $k' = 6.3$ (hexane–ethyl acetate 98:2): ^{1}H NMR ($CDCl_3$): δ 6.05 (dddd, *J* 10.0, 4.4, 2.0, 1.0 Hz, 1 H, CH=C*H*Br), 5.72 (ddm, *J* 10.0, 2.6 Hz, 1 H, CH=C*H*CHOAc), 5.40 (m, *J* 7.0, 2.6, 1.2 Hz, 1 H, C*H*OAc), 4.75 (qdd, *J* 8.2, 1.5, 0.8 Hz, 1 H, C*H*Br), 2.30–1.98 [m, 4 H, (CH$_2$)$_2$], 2.09 (s, 3 H, C*H*$_3$CO$_2$).

trans-**15**: HPLC: $k' = 4.6$ (hexane:ethyl acetate 98:2); ^{1}H NMR ($CDCl_3$): δ 6.15 (ddt, *J* 10.0, 4.7, 1.0 Hz, 1 H, CH=C*H*CHBr), 5.85 (ddt, *J* 10.0, 4.5, 1.1 Hz, 1 H, CH=C*H*CHOAc), 5.31 (qdd, *J* 4.4, 1.8, 0.9 Hz, 1 H, C*H*OAc), 4.80 (qdd, *J* 4.7, 1.8, 0.9 Hz, 1 H, C*H*Br), 2.31–2.03 [m, 4 H, (CH$_2$)$_2$], 2.05 (s, 3 H, CH$_3$CO$_2$).

15': HPLC: $k' = 4.5$ (hexane–ethyl acetate 98:2). ^{1}H NMR (CDCl3): δ 5.89 (ddt, *J* 9.5, 5.1, 2.0 Hz, 1 H, CH=CHBr), 5.79 (dtm, *J* 9.5, 7.2 Hz, 1 H, CH=C*H*CH$_2$), 4.95 (m, 1 H, CHBr), 4.79 (dt, *J* 9.5, 3.6 Hz, 1 H, C*H*OAc), 2.43–2.36 (m, 2 H, C*H*$_2$CH=CH), 2.13–2.04 (m, 1 H, C*H*$_2$CHOAc), 2.13 (s, 3 H, CH$_3$CO$_2$), 1.87–1.76 (m, 1 H, C*H*$_2$CHOAc).

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References

1. Bäckvall, J. E. *Acc. Chem. Res. 16* (1983) 335; *Pure Appl. Chem. 55* (1983) 1669.
2. (a) Bäckvall, J. E., Byström, S. E. and Nordberg, R. E. *J. Org. Chem. 49* (1984) 4619; (b) Bäckvall, J. E., Vågberg, J. and Nordberg, R. E. *Tetrahedron Lett. 25* (1984) 2717; (c) Bäckvall, J. E., Awashi, A. K. and Renko, Z. D. *J. Am. Chem. Soc. 109* (1987) 4750.
3. Bäckvall, J. E., Nyström, J. E. and Nordberg, R. E. *J. Am. Chem. Soc. 107* (1985) 3676.
4. Bäckvall, J. E. and Vågberg, J. O. *J. Org. Chem. 53* (1988) 5695.
5. Bäckvall, J. E., Nordberg, R. E. and Wilhelm, D. *J. Am. Chem. Soc. 107* (1985) 6892.
6. The amount of *p*-benzoquinone can be lowered significantly if MnO_2 is added as an oxidant for hydroquinone (method C).

7. The chloro-alcohol initially formed reacts further to give a mixture of products (via the epoxide) which were not characterized.
8. For a similar example in Pd(0)-catalyzed substitutions, see Fiaud, J. C. and Malleron, J. L. *J. Chem. Soc., Chem. Commun.* (1981) 1159.
9. Magid, R. M. *Tetrahedron 36* (1980) 1901.
10. Colobert, F. and Genêt, J. P. *Tetrahedron Lett. 26* (1985) 2779.
11. Reynolds, W. S., McLean, S., Perpick-Dumont, N. and Enriquez, R. G. *Magn. Reson. Chem. 26* (1988) 1068.
12. Ter Borg, A. P. and Bickel, A. F. *Recl. Trav. Chim. 80* (1961) 1229.
13. Characterized by ^1H NMR and chemical ionization mass spectrometry.
14. The formation of emulsions at this stage can usually be overcome by the addition of $NaBH_4$.

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