Stereo- and Regioselective Palladium-Catalyzed 1,4-Diacetoxylation of 1,3-Dienes

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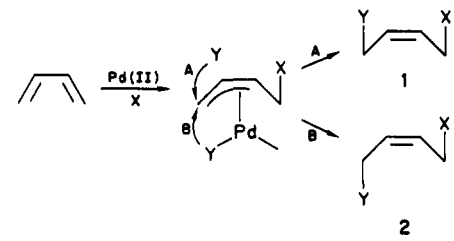
Palladium-catalyzed oxidation of 1,3-dienes in acetic acid using an oxidation system of MnO_2 and catalytic amounts of *p*-benzoquinone selectively gives 1,4-diacetoxy-2-alkenes. The reaction proceeds with high stereo- and regioselectivity, and by ligand control the reaction can be made to take place with either cis or trans 1,4-diacetoxylation across the diene in cyclic systems. Also in an acyclic system the 1,4-relative stereochemistry can be controlled as shown by the stereoselective oxidation of (*E,E*)- and (*E,Z*)-2,4-hexadiene to their corresponding *dl* (>88% *dl*) and meso (>95% meso) diacetates **15** and **18**, respectively. Evidence is provided that supports a mechanism involving a trans acetoxypalladation of the conjugated diene to give an intermediate (π-allyl)palladium complex, followed by either a cis or trans attack by acetate on the allyl group. The cis attack is best explained by a cis migration from a (σ-allyl)palladium intermediate. The diacetoxylation reaction was applied to the preparation of a key intermediate for the synthesis of *dl*-shikimic acid.

Few methods exist for regio- and stereoselective 1,4-addition of oxygen functions to conjugated dienes. The great number of procedures for 1,2-addition of oxygen functions to simple alkenes[1,2] do not generally apply to the 1,4-addition to conjugated dienes. 1,4-Diacetoxylation of 1,3-dienes with moderate selectivity has been described for a few dienes.[3-7] Regio- and stereoselective 1,4-dihydroxylation of 1,3-dienes can be achieved in a few cases via singlet oxygen addition.[8,9] Since 2-alkene-1,4-diol derivatives are important key intermediates in many natural product syntheses,[10-14] more efficient and general methods for their preparation seemed desirable.

Scheme I



We have recently found that 1,3-dienes may be regio- and stereoselectively functionalized in the 1,4-positions via palladium-catalyzed reactions.[15] These 1,4-additions involve an intermediate (π-allyl)palladium complex, which directs the introduction of the second group to the 4-position relative to the first group (Scheme I).[15,16] It is important to control the stereochemistry of the nucleophilic addition of the second group Y to the (π-allyl)palladium intermediate. External trans attack by Y will lead to an overall cis addition across the diene while an intramolecular cis migration will lead to an overall trans addition. It would be very useful to be able to selectively direct a given nucleophile Y toward both pathways. In this way one could obtain either adduct **1** or **2** by choice. A dilemma with this approach is that one class of nucleophiles such as heteronucleophiles and stabilized carbon nucleophiles prefer to attack externally (path A),[15a,e,17,18] whereas another class of nucleophiles such as aryl, alkyl, and hydride nucleophiles only attack via cis migration (path B).[15a,19-21] However, we recently demonstrated that

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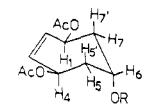
acetate (Y = OAc) can undergo a stereoselective cis migration from palladium to carbon according to path B.[21] We have now found ways of directing the nucleophilic attack by acetate to go either via path A or path B (Scheme I), and in this way obtained stereoselective cis or trans 1,4-diacetoxylations of 1,3-dienes.[22] Importantly, this new reaction allows the control of the 1,4-relative stereochemistry at carbons in both *cyclic* and *acyclic systems*.

Results

Reaction of 1,3-dienes in acetic acid in the presence of palladium acetate (catalytic amounts), *p*-benzoquinone or MnO_2/catalytic *p*-benzoquinone, and lithium salts (LiOAc, catalytic LiCl) proceeds smoothly to selectively produce 1,4-diacetoxy-2-alkenes (Table I). The reaction conditions are very mild and most reactions were performed at room temperature. There is a remarkably high regioselectivity for 1,4-addition for all dienes studied, which except for a few cases (entries 5 and 14–17) is 97–100%. 1,3-Cyclooctadiene, which shows a moderate regioselectivity in a related 1,4-addition,[15d] gave a ratio 1,4-addition:1,2-addition of approximately 90:10 (entries 14 and 15), and trans diacetoxylation of 2-methyl-1,3-cyclohexadiene gave a 1,4:1,2 ratio of 5:1 (entry 5). When both double bonds are terminal (butadiene, isoprene), a lower selectivity for 1,4-addition was also observed (entries 16 and 17). In the initial stage of our study we used 2 equiv of *p*-benzoquinone as the oxidant. This procedure suffered from a competing Diels–Alder addition between the benzoquinone and the diene and was not synthetically useful for the oxidation of acyclic 1,3-dienes. In an improved procedure we have overcome this problem by using *p*-benzoquinone in catalytic amounts in combination with an external oxidant such as manganese dioxide. *p*-Benzoquinone is required for the high selectivity and appears to work as a ligand (vide infra). Also when a two-phase system of a hydrocarbon (pentane or hexane) and acetic acid is used, the diene substrate is slowly fed into the acetic acid phase, which depresses the competing Diels–Alder reaction.

For 1,3-cyclohexadiene the 1,4-diacetoxylation takes place in high yield and, more importantly, by a slight change in the ligand concentrations either the cis diacetate **3** or the trans diacetate **4** can selectively be obtained (entries 2 and 3, Table I). Thus in the presence of catalytic amounts of LiCl only the cis diacetate **3** (>96% cis) was formed, whereas in the absence of LiCl the trans diacetate **4** (>91% trans) is the product. Also, for some other cyclic 1,3-dienes (entries 4, 5, 7, 8, 10, 11, 14, and 15) it was possible to obtain this dual stereoselectivity in the 1,4-diacetoxylation. Cyclopentadiene, however, gave only the cis isomer under all conditions tried. The reason for the unwillingness of cyclopentadiene to undergo a trans diacetoxylation will be discussed below.

Several substituted cyclic 1,3-dienes were studied to determine the scope of the diacetoxylation reaction. In particular the directing effect of an allylic or homoallylic substituent is of interest for the diastereoselectivity of the reaction. The most clearcut result was obtained for the cis diacetoxylation of cyclic dienes **5** (entries 12 and 13),

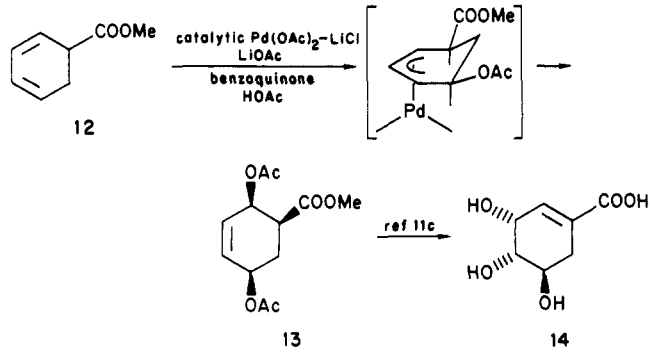


6a (R = CH_3CO): $J_{56} = J_{67} = 4.5$ Hz; $J_{5'6} = J_{67'} = 4.5$ Hz; $J_{45'} = J_{17'} = 10$ Hz; $J_{45} = J_{17} = 4$ Hz

6b (R = CH_3): $J_{56} = J_{67} = 5.5$ Hz; $J_{5'6} = J_{67'} = 3.0$ Hz; $J_{45'} = J_{17'} = 11$ Hz; $J_{45} = J_{17} = 2.5$ Hz

Figure 1.

Scheme II



which in each case gave only one isomer according to ^1H NMR, GLC, and HPLC. From the ^1H NMR spectra of products **6** they were assigned as 1β,4β,6α-triacetoxy-2-cycloheptene (**6a**) and 1β,4β-diacetoxy-6α-methoxy-2-cycloheptene (**6b**). Thus, for **6a** the magnitude of the coupling constants, J_{56} (= J_{67}) ≈ $J_{5'6}$ (= $J_{67'}$) = 4.5 Hz, $J_{45'} = J_{17'} = 10$ Hz, and $J_{45} = J_{17} = 4$ Hz, are best explained by the conformations shown in Figure 1, in which the 6-acetoxy group is trans to the other two acetoxy groups.[23] In this arrangement the protons H_1, H_4, $H_{5'}$, and $H_{7'}$, become pseudoaxial, whereas protons H_5 and H_6 and H_7 become pseudoequatorial. This would give a large $J_{45'}$ coupling but small J_{56} and $J_{5'6}$ couplings, which is observed. The same magnitude of coupling constants was also observed for the product **6b**.

Diacetoxylation of 1-methyl-, 2-methyl-, and 5-methyl-1,3-cyclohexadiene, using the chloride free procedure, gave in each case a stereoselective trans addition (entries 6, 5, and 8, Table I). The trans 1,4-diacetoxylation of 1-methyl-1,3-cyclohexadiene in 70% yield shows that the diene may be fully substituted on at least one of the sites for acetate attack. In the presence of catalytic amounts of LiCl, 2-methyl- and 5-methyl-1,3-cyclohexadiene gave a stereoselective cis 1,4-diacetoxylation (entries 4 and 7), while 1-methyl-1,3-cyclohexadiene reacted sluggishly and produced a 1:1 mixture of cis and trans products. Cis 1,4-diacetoxylation of 5-methyl-1,3-cyclohexadiene (**7**) afforded two isomers (**8** and **9**) in comparable amounts (entry 7), showing that the methyl group has a minor directing effect on the diacetoxy groups introduced in this case. Trans 1,4-diacetoxylation of diene **7** resulted in a 3:1 mixture of isomers **10** and **11**, contaminated with 9% of the cis-addition product **9** (entry 8). In this way all of the four possible isomers of 5-methyl-2-cyclohexene-1,4-diol are available in pairs of two. The assignment of the isomers **8**, **9**, **10**, and **11** was made by ^1H NMR spectroscopy (see Experimental Section) and is based on the fact that the methyl substituent preferentially will possess an equatorial position.[24] The product mixtures obtained from the diacetoxylations of **7** reflect the nonselective coordination of palladium to the diene. Acetoxypalladation of diene **7** apparently results in several

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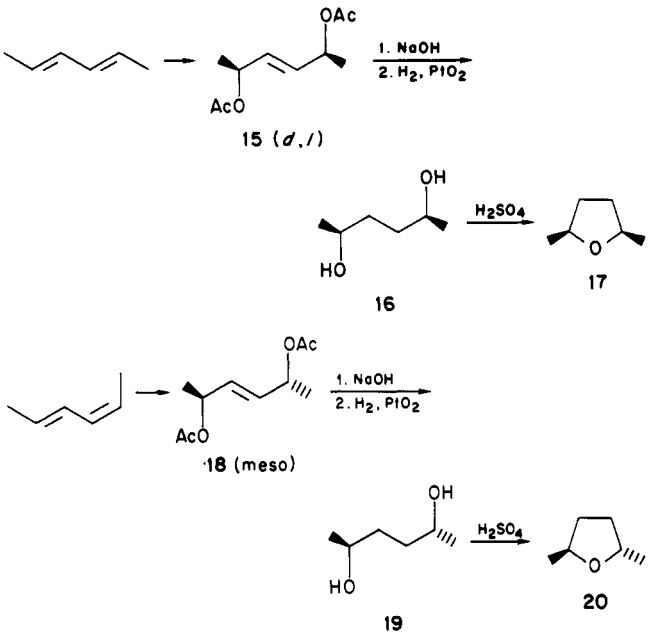
Scheme III



isomeric (π-allyl)palladium intermediates (vide infra).

Palladium-catalyzed diacetoxylation of diene **12**, using the conditions for cis addition, was stereoselective and gave mainly the β,β,β isomer **13**,[11d] which was isolated in 59% yield. Compound **13** is a key intermediate for the synthesis of *dl*-shikimic acid **14** (Scheme II).[11] The ^{1}H NMR and HPLC of **13** showed the presence of another isomer in small amounts. From the ^{1}H NMR of this isomer we have assigned it as the $1\beta,4\beta,5\alpha$ isomer of **13**.[11d]

Acyclic conjugated dienes were oxidized to their corresponding 1,4-diacetates in moderate to good yields (entries 16–22, Table I). In general the reaction of acyclic dienes is slower than the corresponding oxidation of cyclic dienes, and the competing Diels–Alder reaction becomes more important. The experimental procedure is therefore much simplified by the use of the two-phase system (acetic acid–pentane or hexane), which keeps the diene concentration low in the acetic acid phase throughout the reaction. Except for butadiene, acyclic dienes also show a high selectivity for formation of the 1,4-isomer. Furthermore, the double bond formed was only or predominantly of *E* configuration. Isoprene gave a 1,4-diacetate with an *E*:*Z* ratio of 5.5:1, while the other acyclic dienes investigated gave 1,4-diacetoxy-2-alkenes of almost exclusively *E* configuration (94–100%).

The 1,4-diacetoxylation of 2,4-hexadiene can in principle give four different diastereoisomers. If the olefin geometry of the product 2,5-diacetoxy-3-hexene is of *E* configuration, two possible diastereoisomers (meso and *dl*) may form. Palladium-catalyzed oxidation of (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene, utilizing the procedure with chloride ligands, gave in each case one diastereoisomer as the main product, and importantly, the diacetate from the (*E*,*E*)-diene differed from the one from the (*E*,*Z*)-diene (Scheme III). Furthermore in both diacetates **15** and **18** the double bond was of *E* configuration. Consequently, they must have different 1,4-relative configuration. This shows that the diacetoxylation is stereoselective also for acyclic 1,3-dienes and that it is possible to control the relative stereochemistry at distant carbons in an acyclic system.[25] The diacetates **15** and **18**, obtained from (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene respectively, could not be assigned directly by spectroscopic methods. They showed essentially identical ^{1}H NMR spectra at 200 MHz, but their ^{13}C NMR spectra were slightly different. The assignments and stereochemical analysis of **15** and **18** were made according to the sequence shown in Scheme III. Hydrolysis and subsequent hydrogenation gave the known[26] 2,5-hexanediols **16** and **19**. In order to obtain a more accurate stereochemical analysis, the diols **16** and **19** were cyclized to their corresponding tetrahydrofurans by treatment with H_2SO_4.[27] This cyclization, which involves one inversion, converts the *dl* diol into *cis*-2,5-dimethyltetrahydrofuran (**17**) and the meso diol into *trans*-2,5-dimethyltetrahydrofuran (**20**). Analyses of the cyclized products by ^{1}H NMR spectroscopy showed that the tetrahydrofuran **17** obtained from **15** via **16** was mainly cis (cis:trans = 83:17) and that the tetrahydrofuran **20** obtained from **18** via **19** was mainly trans (cis:trans = 12:88). This establishes that the diacetate **15** from (*E*,*E*)-2,4-hexadiene is the *dl* isomer and that the diacetate **18** from (*E*,*Z*)-2,4-hexadiene is the meso isomer. From the ^{13}C NMR spectra of **15** and **18** it was determined that **15** has a *dl*:meso ratio of 88:12 and that **18** is >95% meso. It thus appears that a slight isomerization occurs during the hydrogenation step in Scheme III.

Because of the tendency of *p*-benzoquinone to undergo Diels–Alder reactions we tried to replace it by other oxidants. A range of different oxidants such as copper(II) salts, MnO_2, CrO_3, $Ce(SO_4)_2$, $Pb(OAc)_4$, $Tl(OAc)_3$, $LiNO_3$, isoamyl nitrite, and substituted benzoquinones were tried. All of these oxidants were either very inefficient or gave a slower and less selective reaction in the 1,4-diacetoxylation. Although $Tl(OAc)_3$ and $Pb(OAc)_4$ have been reported to decompose (π-allyl)palladium complexes to allylic acetates,[28] the former was completely unable to promote a catalytic reaction and the latter gave a poor result (Table II). Urea hydroperoxide, however, worked fairly well, but the stereo- and regioselectivity of the reaction was lower than the reaction with *p*-benzoquinone. The unique ability of *p*-benzoquinone to work as a selective and efficient oxidant in the 1,4-diacetoxylation is puzzling, but a likely explanation is that it also serves as a ligand.[29,30]

We therefore tried to use *p*-benzoquinone in catalytic amounts in combination with an external oxidant. Cerium(IV) sulfate or $Tl(OAc)_3$ in combination with catalytic amounts of *p*-benzoquinone worked to some extent, but a better result was obtained with MnO_2 as the external oxidant (Table II). Equimolar amounts of commercial MnO_2 together with catalytic amounts of *p*-benzoquinone gave a very efficient reaction and 1,3-cyclohexadiene was oxidized to 1,4-diacetoxy-2-cyclohexene (trans:cis = 91:9) in almost quantitative yield by using the chloride free procedure. Manganese dioxide itself (without added benzoquinone) gave a very slow diacetoxylation (Table II).

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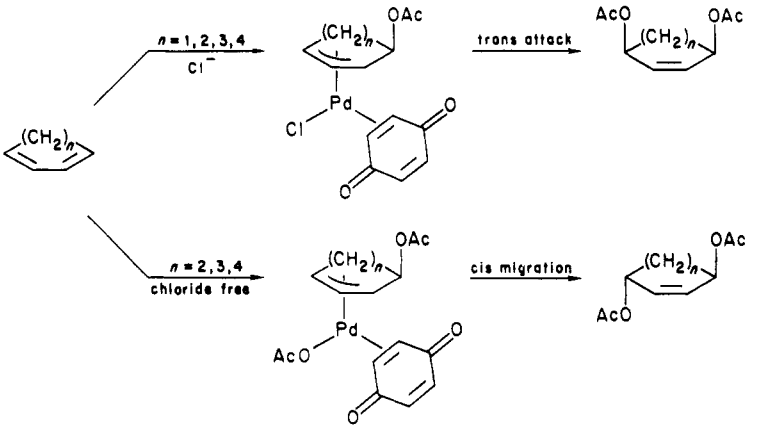
Scheme IV



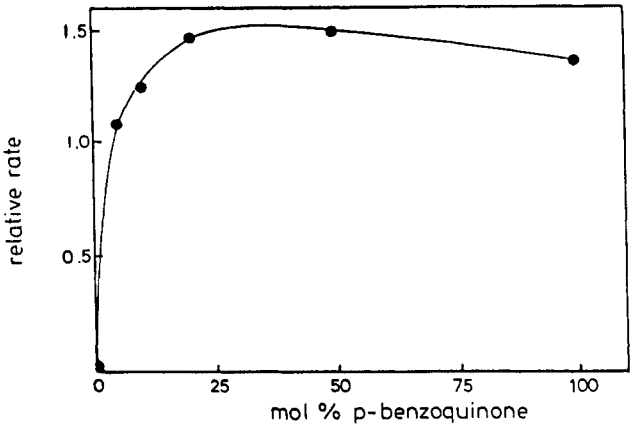


Figure 2. Relative initial rate of palladium-catalyzed 1,4-diacetoxylation of 1,3-cyclohexadiene in chloride-free acetic acid at different concentrations of *p*-benzoquinone using 100 mol % MnO_2.

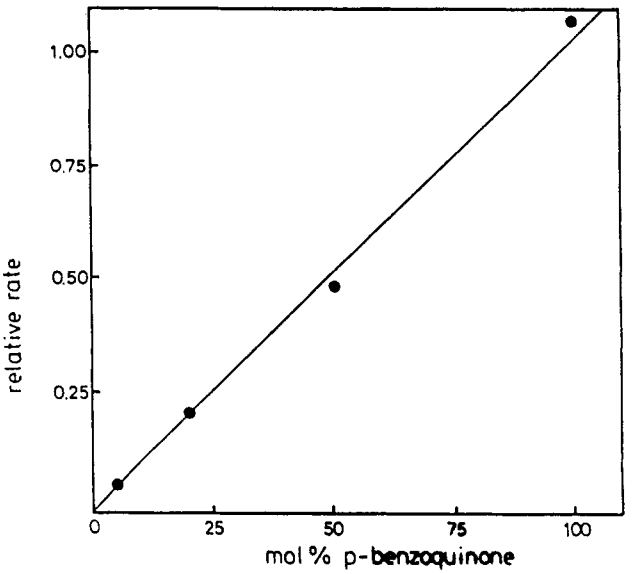


Figure 3. Relative initial rate of palladium-catalyzed 1,4-diacetoxylation of 1,3-cyclohexadiene in acetic acid in the presence of chloride ligands ($Pd(OAc)_2$:LiCl = 1:4) at different concentrations of *p*-benzoquinone using 100 mol % MnO_2.

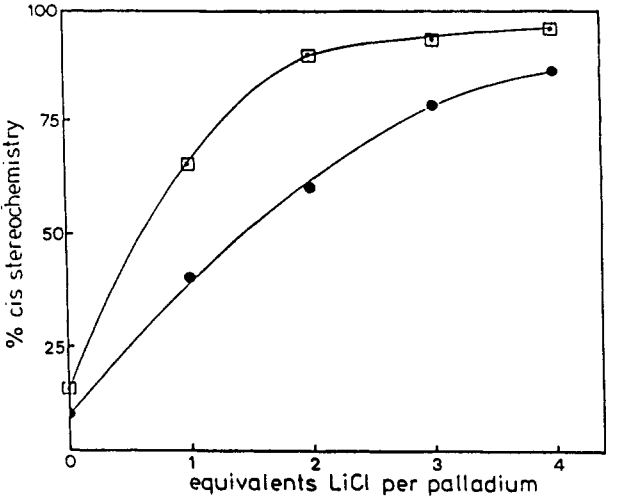


Figure 4. Stereochemistry of the 1,4-diacetoxylation of 1,3-cyclohexadiene as a function of the amount of added LiCl at constant acetate concentration. Squares, [LiOAc] = 2 M; circles, [LiOAc] = 0.6 M ([$Pd(OAc)_2$] = 0.03 M (5 mol %)). The cis to trans ratio of the diacetate was determined by ^1H NMR spectroscopy and checked by HPLC.

Addition of only 5 mol % of *p*-benzoquinone resulted in a tremendous increase in the oxidation rate. Interestingly, addition of more benzoquinone led only to a moderate increase of the rate, and addition of more than 30% benzoquinone gave no significant increase of the reaction rate (Figure 2). In contrast to this observation the rate of the 1,4-diacetoxylation in the presence of LiCl is almost proportional to the concentration of *p*-benzoquinone. The rate of the cis 1,4-diacetoxylation of 1,3-cyclohexadiene as a function of the benzoquinone concentration is plotted in Figure 3 and shows an almost linear dependence on *p*-benzoquinone up to 100 mol %.

We also tried other quinones in catalytic amounts in combination with MnO_2. Methyl- and methoxy-substituted *p*-benzoquinones gave in the chloride free case a much slower and less selective reaction. The selectivity decreased with increased substitution of the quinone (Table III).

To obtain further insight into the mechanism of the diacetoxylation, we studied the stereochemistry of the diacetoxylation as a function of the chloride and acetate concentrations (Figures 4 and 5).

Discussion

It is likely that the overall cis stereochemistry observed for cyclic 1,3-dienes in the presence of chloride ligands is a result of a trans acetoxypalladation of one of the double bonds, followed by an external trans attack by acetate on an intermediate (π-allyl)palladium complex (Scheme IV). Analogously, the products obtained in the chloride free case would be explained by a trans acetoxypalladation of one of the double bonds of the diene and subsequent cis migration of coordinated acetate from palladium to the allyl group (Scheme IV). This migration may take place via either a π-allyl or a σ-allyl intermediate. In principle

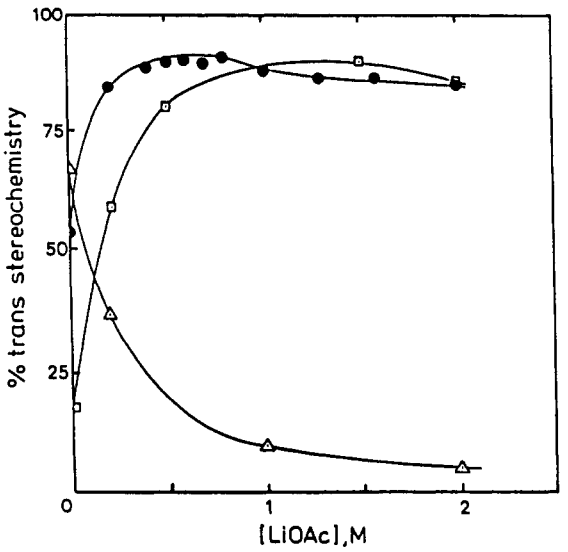
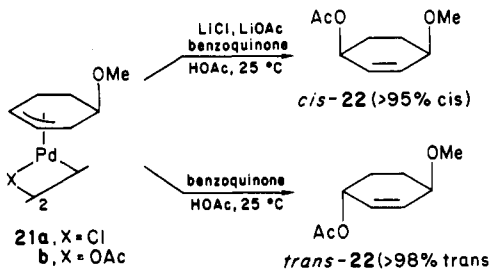


Figure 5. Stereochemistry of the 1,4-diacetoxylation of cyclic dienes as a function of the lithium acetate concentration in chloride-free acetic acid. *p*-Benzoquinone was used as the oxidant. The stereochemistry of the 1,4-diacetate was determined by ^{1}H NMR spectroscopy and/or HPLC (●) 1,3-cyclohexadiene; (△) 1,3-cycloheptadiene; (□) 1,3-cyclooctadiene.

Scheme V



a cis acetoxypalladation of the diene followed by an external acetate attack would give the same result in the latter case. Such a pathway can, however, be ruled out on the basis of several observations. Although cis oxypalladation of a strained conjugated diene has recently been reported,[31] the oxypalladation of 1,3-cyclohexadiene has been observed to proceed with trans stereochemistry.[21] Furthermore, it has been shown that acetoxypalladation of olefins in acetic acid occurs trans,[32] even in the absence of chloride ion ligands.[32b] Finally and most convincingly, acetate attack on the (π-allyl)palladium complex **21** related to the putative intermediate in the catalytic reaction, occurs cis in the absence of chloride but trans in the presence of chloride (Scheme V).[15c] Although oxidative decomposition of (π-allyl)palladium complexes to allylic acetates has previously been reported,[28,33] the reactions in Scheme IV represent the first example where a nucleophilic addition to a (π-allyl)palladium can be completely sterically controlled.

The role of the catalytic amounts of lithium chloride in the palladium-catalyzed diacetoxylation seems to be to block the coordination of acetate and in this way inhibit a cis migration pathway.[15c] Figure 4 shows the stereochemical outcome of the 1,4-diacetoxylation of 1,3-cyclohexadiene on variation of the chloride ion concentration. As can be seen from the figure, an increase of the lithium chloride ion concentration from 0 to 4 equiv per palladium at constant lithium acetate concentration drastically changes the stereochemistry of the product from mainly trans to mainly cis. A similar but less pronounced ligand effect was observed for acetate anion in the chloride ion free case. The stereochemistry of the diacetoxylation of 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene as a function of the acetate concentration in chloride free acetic acid is shown in Figure 5. In the absence of acetate, 1,3-cyclohexadiene and 1,3-cycloheptadiene gave approximately 1:1 and 1:2 mixtures of cis and trans diacetates, whereas 1,3-cyclooctadiene predominantly yielded the cis diacetate (cis:trans = 83:17). Increasing the acetate concentration drastically changed the stereochemistry of the reaction in each case. The six- and eight-membered rings now mainly afforded the trans isomers, whereas the seven-membered ring selectively gave the cis isomer. Further increase of the acetate concentration above 1 M for 1,3-cyclohexadiene and above 1.5 M for 1,3-cyclooctadiene led to a slight depression of the selectivity for the trans isomer.

The above-mentioned experiments show the importance of the ligand concentration in controlling the stereochemistry of the reactions. The balance between the external trans attack and a cis migration can be drastically affected by a change in the ligand environment. Similar ligand effects, but weaker, have been observed[34] in palladium-catalyzed alkylations of allylic acetates, which proceed via (π-allyl)palladium intermediates.[35] Increasing the triphenylphosphine concentration increased the stereospecificity from 79% to 98% overall retention in the alkylation, most likely by blocking the coordination of acetate to palladium and thus preventing the isomerization of the starting material.

The role of *p*-benzoquinone seems to be not only to serve as an oxidant but also to act as a ligand. Stable *p*-benzoquinone complexes of nickel(0), palladium(0), and platinum(0) are well-known,[29] and protonation of a (*p*-benzoquinone)nickel(0) complex has been shown to yield hydroquinone and nickel(II).[29c] Also kinetic studies indicate that *p*-benzoquinone coordinates to palladium(II) in a (π-allyl)palladium complex.[30]

The results from the effect of *p*-benzoquinone on the rate of the diacetoxylation (Figures 2 and 3) are best explained by a coordination of benzoquinone (BQ) to palladium (eq 1). In the chloride free case (**23a**) it is easy

$$\underset{\textbf{23a, b}}{\text{(allyl)PdX}_2^-} + \text{BQ} \rightleftarrows \underset{\textbf{24}}{\text{(allyl)Pd(BQ)X}} + \text{X}^- \quad (1)$$

for benzoquinone to coordinate to palladium, since acetate is a weakly coordinating ligand that is readily displaced. In this case the equilibrium (eq 1) is shifted to the right and only a moderate concentration of benzoquinone is required to transform almost all **23a** into the reactive complex **24**. This occurs at about 30 mol % of benzoquinone in our case (cf. Figure 2), and increasing the benzoquinone concentration beyond this point will not significantly increase the concentration of **24** and hence the rate of the reaction. On the other hand, when chloride is the counterion to palladium (**23b**) the picture is changed and now the rate of the reaction increases linearly with the *p*-benzoquinone concentration (Figure 3). Chloride ion is a much stronger coordinating ligand than acetate and now

(31) Hosokawa, T.; Imada, Y.; Murahashi, S. I. *Tetrahedron Lett.* **1982**, *23*, 3373.
(32) (a) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 1494. (b) Andell, O. S.; Bäckvall, J. E. *J. Organomet. Chem.* **1983**, *244*, 401.
(33) Wolfe, S.; Campbell, P. G. C. *J. Am. Chem. Soc.* **1971**, *93*, 1499.
(34) Trost, B. M.; Verhoeven, T. *J. Am. Chem. Soc.* **1980**, *102*, 4730.
(35) (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer Verlag: Berlin, 1980. (c) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

Table I. Palladium-Catalyzed 1,4-Diacetoxylation of 1,3-Dienes[a]

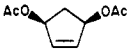
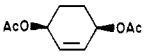
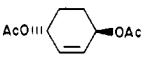
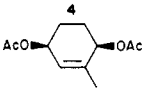
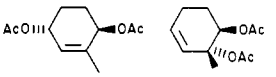
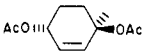
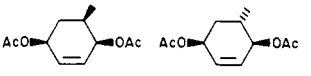
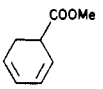
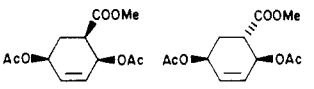
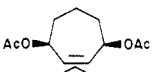
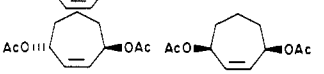
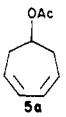
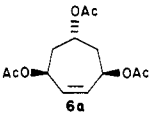
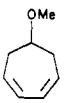
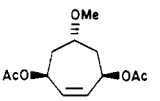
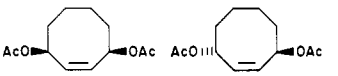
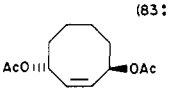
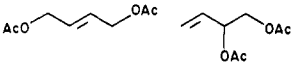
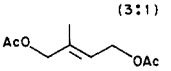
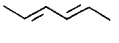
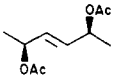
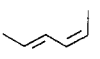
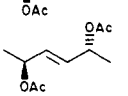
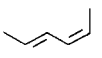
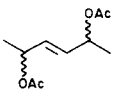
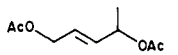
entry	diene	LiOAc	LiCl[b]	product	yield,[c] %	stereochemistry
1		yes	yes[d]		40[e]	>98% cis
2		yes	yes	 **3**	85	>96% cis
3		yes	no	 **4**	93	>91% trans
4		yes	yes		51	>95% cis
5		yes	no	 (5:1)	71	>91% trans
6		yes	no		70	>95% trans
7	 **7**	yes	yes	 **8** **9** (1.4:1)	69	*f*
8	 **7**	yes	no	 **10** **11** (3:1)	85	*g*
9		yes	yes	 (9:1)	59	
10		a, yes b, yes	yes no		70 85	>98% cis >95% cis
11		no	no	 (66:34)	68[h]	
12	 **5a**	a, yes b, yes	yes no	 **6a**	70 78	>95% 1β,4β,6α
13	 **5b**	yes	no	 **6b**	89	>95% 1β,4β,6α
14		no	no	 (83:17)	50[e,i]	
15		yes	no		56[e,i]	trans:cis = 90:10
16		yes	no	 (3:1)	49	*E*/*Z* = 94:6 for 1,4-isomer
17		yes	no		30[e,i]	*E*/*Z* = 5.5:1
18		yes	no		40[h,j]	>88% *dl*
19		yes	yes		51[e,j]	>95% meso
20		yes (high)	no		89[e,j]	*dl*/meso = 60:40
21		yes (low)	no		76[e,j]	*dl*/meso = 70:30

Table I (Continued)

entry	diene	LiOAc	LiCl[b]	product	yield,[c] %	stereochemistry
22		yes	no		29[e,j]	

[a] Unless otherwise noted the reaction was performed in acetic acid at room temperature or slightly above room temperature using 5 mol % of $Pd(OAc)_2$ as catalyst (see Experimental Section). [b] Catalytic amounts of LiCl except for entry 1. [c] Isolated yield. [d] 3.5 equiv of LiCl to diene was used in this case. [e] 8 mol % of $Pd(OAc)_2$. [f] Contains less than 5% of **10** and **11** together. [g] Contaminated with 9% of **9** [h] 10 mol % of $Pd(OAc)_2$. [i] Contains ~10% of the 1,2-isomer. [j] >95% 1,4-isomer and only the *E* isomer was observed.

Scheme VI

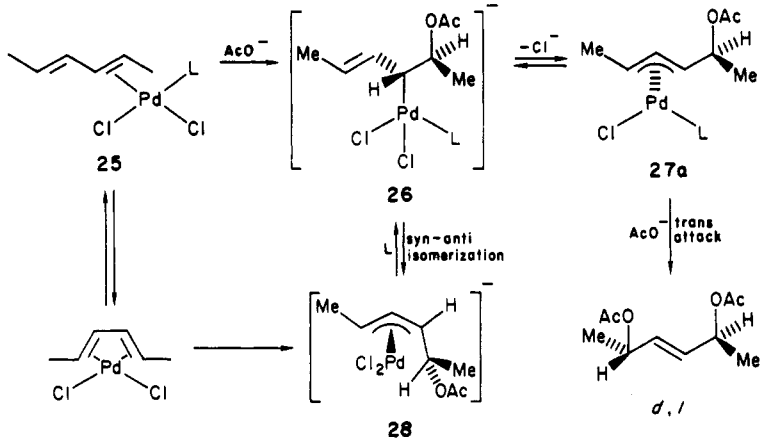


Table II. Effect of Catalytic Amounts of *p*-Benzoquinone in the Palladium-Catalyzed Oxidation of 1,3-Cyclohexadiene[a]

oxidant[b]	% yield of 1,4-diacetate (trans/cis)	% selectivity for 1,4-diacetate
MnO_2	3	*c*
$Tl(OAc)_3$	4	45
$Pb(OAc)_4$	17 (62/38)	37
MnO_2/catalytic BQ	92 (91/9)	>99
$Tl(OAc)_3$/catalytic BQ	74 (91/9)	>99
$Pb(OAc)_4$/catalytic BQ	42 (84/16)	77

[a] 8 h of reaction time. [b] BQ = *p*-benzoquinone (20 mol % was used). [c] Not determined.

Table III. Palladium-Catalyzed Oxidation of 1,3-Cyclohexadiene with MnO_2 and Catalytic Amounts of Quinones

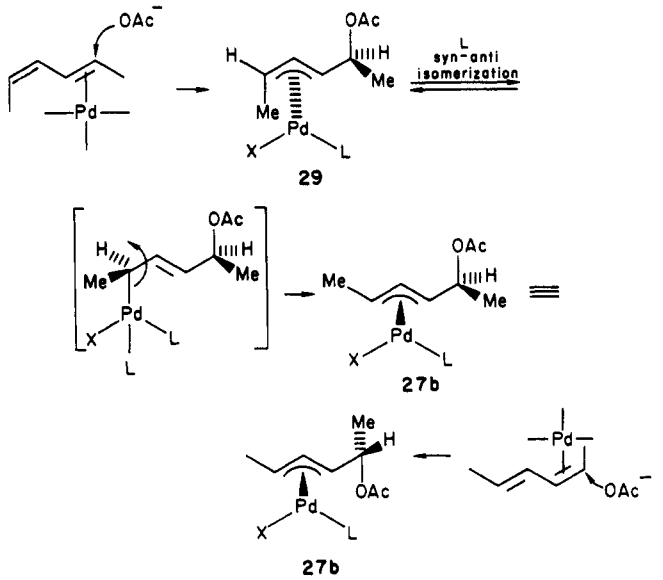
	trans/cis ratio of 1,4-diacetoxy-2-cyclohexene	reactn time, h	yield,[a] %
1,4-benzoquinone	91/9	8	93
2,6-dimethyl-1,4-benzoquinone	83/17	72	90
2-methyl-1,4-naphthoquinone	83/17	72	55
chloranil	81/19	48	50
1,2-benzoquinone[b]	70/30	60	90
2,3,5,6-tetramethyl-1,4-benzoquinone	63/37	72	81
2,6-dimethoxy-1,4-benzoquinone	54/46	72	72

[a] Isolated yield. [b] Generated in situ from *o*-catechol.

the equilibrium will be much shifted to the left. The concentration of the reactive complex **24** will therefore increase approximately linearly with the concentration of *p*-benzoquinone since the chloride concentration can be considered as essentially constant.

The control of the 1,4-relative stereochemistry in the acyclic systems can be explained according to Scheme VI. Trans acetoxypalladation of one of the double bonds in

Scheme VII



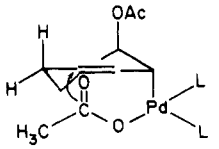
the η^2-(*E,E*)-diene complex **25** gives the *syn*-(π-allyl)palladium complex **27a**, possibly via the σ-complex **26a**. External trans attack on **27a** would produce the observed *dl* diacetate of *E* double-bond configuration. If a cis-coordinated η^4-diene complex is involved, the stereochemical result will be the same, provided syn–anti isomerization **27a** ⇄ **28** is rapid. The high selectivity for *E*-meso product **18** from (*E,Z*)-diene (and *E-dl* product **15** from (*E,E*)-diene) relies on the fact that **27a** is more stable than **28**. Provided syn–anti isomerization is fast enough, (*E,Z*)-2,4-hexadiene would give only one π-allyl intermediate (**27b**), independent of which one of the two double bonds that are attacked first (Scheme VII). Complex **27b** is diastereomeric with **27a** in Scheme VI. In the isomerization **29** ⇄ **27b** palladium moves from one face to the other of the π-allyl group and the result is inversion at C-3 in the (2-acetoxy-3-5-η^3-hexenyl)palladium complex. The configuration at C-2 and C-5, however, is unchanged, and

therefore the product is the same whether the trans attack by acetate takes place on **29** or **27b**, although the latter seems more likely.

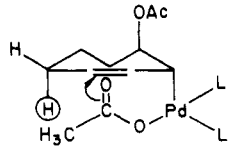
(π-Allyl)palladium complexes analogous to **27** has previously been prepared by chloropalladation of 2,4-hexadiene.[36] It was found that (*E,E*)- and (*E,Z*)-2,4-hexadiene gave (2-chloro-3-5-η^3-hexenyl)palladium complexes that were diastereomeric to one another. Furthermore, (*Z,Z*)-2,4-hexadiene gave the same diastereoisomer as obtained from (*E,E*)-2,4-hexadiene. This supports the mechanism outlined in Scheme VI and VII for the diacetoxylation of 2,4-hexadienes.

The arguments inferred in Scheme VII show that syn–anti isomerization at one of the centers of the π-allyl group (**27b** $\rightleftarrows$ **29**) does not affect the stereochemical outcome of the diacetoxylation. Syn–anti isomerization at the other center, e.g., **27a** $\rightleftarrows$ **28**, certainly changes the configuration at C-5, but attack by acetate would give only the *Z* isomer of the meso compound. The slight loss of stereospecificity in the oxidation of 2,4-hexadienes is therefore not readily rationalized by syn–anti isomerizations. A control experiment showed that the 2,4-hexadienes do not undergo *E–Z* isomerization under the reaction conditions. The slight loss of the stereospecificity is probably due to a competing cis migration of acetate in the intermediate (π-allyl)palladium complex. By a change in the ligand environment (no LiCl, low LiOAc), it was possible to obtain a *dl*:meso ratio of 70:30 from (*E,Z*)-2,4-hexadiene, which indicates that cis migration of acetate to the π-allyl group now predominates.

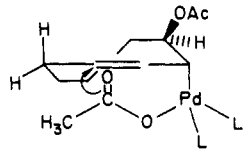
The observed difference in stereochemistry between the diacetoxylation of the five-, six-, seven-, and eight-membered rings in chloride free acetic acid deserves some comment. Thus, for 1,3-cyclohexadiene and 1,3-cyclooctadiene, the trans diacetate can be made the main product. For 1,3-cycloheptadiene the highest relative yield of the trans isomer is trans:cis = 66:34, and for cyclopentadiene the trans diacetate was not formed under any conditions. This suggests that cis migration of acetate is facile from the (allyl)palladium intermediates of the six- and eight-membered rings but more difficult from the (allyl)palladium intermediates of the five- and seven-membered rings. If one assumes that the cis migration preferentially occurs through a (σ-allyl)palladium complex,[21,35c] these observations may be explained by conformational differences in the ring systems. As can be seen from the assumed (σ-allyl)palladium intermediates **30** and **31** from 1,3-cyclohexadiene and 1,3-cycloheptadiene, a cis migration would be less favored from **31** due to steric interactions with the pseudoaxial allylic hydrogen. The



30



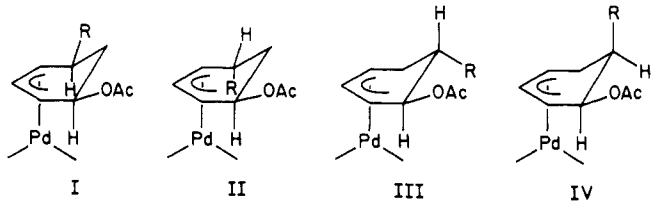
31



32

(cyclopentenyl)palladium complex shows an analogous steric interaction as the cycloheptenyl complex, and because of the ring strain a cis migration would be even more unfavored in the five-membered ring system. The cyclooctenyl system is more difficult to analyze, but one can find at least one (σ-allyl)palladium conformation, **32**, which gives a comparable interaction in the cis migration as the cyclohexenyl system.

Scheme VIII

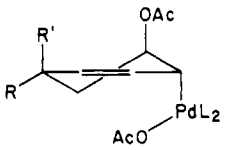


external attack (R = Me)
I or IV → **8** (1β,4β,5β)
II or III → **9** (1β,4β,5α)

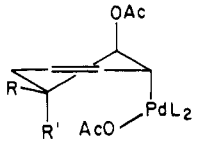
cis migration (R = Me)
II or IV → **10** (1α,4β,5β)
I or III → **11** (1α,4β,5α)

The change of stereochemistry in each case in Figure 5 on variation of the acetate concentration is less obvious. In the six- and eight-membered rings one may rationalize the initial increase of trans product by a need of coordination of acetate for a cis migration. At higher acetate concentration the external attack by acetate would compete and favor formation of cis product. It should be mentioned that the chloride free case in acetic acid is complicated since dimeric as well as trimeric species of palladium(II) acetate may be involved.[37]

The results obtained from the diacetoxylation of 5-methyl-1,3-cyclohexadiene also support a mechanism involving a (σ-allyl)palladium intermediate in the cis migration of acetate. The four possible (π-allyl)palladium complexes from 5-methyl-1,3-cyclohexadiene are shown in Scheme VIII. It is likely that these complexes can equilibrate with one another via free diene through a reversible acetoxypalladation. Of the complexes shown in Scheme VIII, I and III should be more favored from a conformational point of view, with both substituents in pseudoequatorial positions. Complexes I and III are probably the principal intermediates in the reaction involving external trans attack.[38] The product distribution in the trans diacetoxylation involving the cis migration is less obvious from considering the (π-allyl)palladium complexes I–IV. It appears that the major product **10** has



σ-II, R = Me; R' = H
σ-I, R = H; R' = Me



σ-IV, R = Me; R' = H
σ-III, R = H; R' = Me

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(38) Good support for complexes I and III as the major intermediates in the *cis*-1,4-diacetoxylation follows from the product distribution obtained in the analogous palladium-catalyzed 1,4-acetoxychlorination reaction of 5-methyl-1,3-cyclohexadiene. The latter reaction, which involves external attack by chloride on an intermediate (π-allyl)palladium complex,[15d] gave 1β-acetoxy-4β-chloro-5β-methyl-2-cyclohexene and 1β-chloro-4β-acetoxy-5α-methyl-2-cyclohexene as the major products in 45% and 34% relative yields, respectively. The chloroacetates expected from complexes I, II, III, and IV were formed in a ratio of 45:12:34:9; Nordberg, R. E., unpublished results from this laboratory.

been formed via one of the less favored complexes II or IV or both. However, by assuming that the cis migration takes place through a σ-allyl intermediate, the observed results can be rationalized. Thus, a reaction through σ-II and σ-IV becomes a lower energy pathway than that through σ-I or σ-III, since the methyl groups in the former become pseudoequatorial, whereas the methyl groups in σ-I and σ-III become pseudoaxial. The fact that **10** is the major product from trans diacetoxylation of 5-methyl-1,3-cyclohexadiene is therefore consistent with a cis migration via a (σ-allyl)palladium intermediate.

The high diastereoselectivity in the cis diacetoxylation of 5-carbomethoxy-1,3-cyclohexadiene (**12**) is understandable in view of the above arguments, since complex I (R = COOMe) will be more favored in this case.

The high diastereoselectivity in the cis diacetoxylation of **5** to give exclusively one diastereoisomer **6** is probably an effect of coordination of palladium from the less hindered convex side of the molecule.[15b]

Synthetic Utility of the 1,4-Diacetoxylation. Many 2-alkene-1,4-diol derivatives are important synthetic intermediates. The diacetate obtained from cyclopentadiene (entry 1) is an often used intermediate for natural product synthesis,[10,12d,14] in particular for prostaglandin synthesis.[10] Although the yield of *cis*-1,4-diacetoxy-2-cyclopentene is moderate, the high stereoselectivity and the difficulties of obtaining this substance by other methods should make our procedure for its preparation synthetically useful. As exemplified in Scheme II, we have used the diacetoxylation to prepare a key intermediate for *dl*-shikimic acid synthesis. The fact that diene **12** in Scheme II is readily available on a large scale in one pot from 4-carbomethoxycyclohexene enhances the utility of this strategy.[39] Both *cis*- and *trans*-1,4-diacetoxy-2-cyclohexene and their diols are useful building blocks[21a] and to our knowledge this is by far the simplest method for their preparation on a large scale (≈ 10 g).

The fact that the allylic oxygen groups can be substituted by using transition-metal (Pd, Cu, Ni, Mo, Fe) catalysis[35,40] enhances the synthetic utility of the diacetoxylation reaction. We have shown that the diacetoxylation indirectly allows a two-step stereoselective cis or trans 1,4-diamination of 1,3-cyclohexadiene, by applying a palladium-catalyzed amination on the diacetates **3** and **4**.[15b,41] In the acyclic series 2-alkene-1,4-diol derivatives have found application for the synthesis of vinylcyclopropane derivatives related to chrysanthemic acid.[42] Selective palladium-catalyzed amination of acyclic 2-alkene-1,4-diol diacetates or monoacetates was used as a synthetic route to 1,4-amino alcohol derivatives.[43]

Concluding Remarks

Palladium-catalyzed 1,4-diacetoxylation of 1,3-dienes leads to regio- and stereoselective formation of 1,4-diacetoxy-2-alkenes. Through this work many of these synthetically important 2-alkene-1,4-diol derivatives are now readily accessible. In particular the method allows the control of the 1,4-relative stereochemistry at carbons and enables the selective preparation of both cis and trans isomers in cyclic systems as well as *R*R** (e.g., *dl*) and *R*S** (e.g., meso) isomers in acyclic systems. In view of the great number of stereoselective synthesis of conjugated dienes recently developed,[44,45] the present diacetoxylation procedure should have a great potential in organic synthesis.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 421 spectrometer. All NMR spectra reported were obtained with a Bruker WP 200 FT spectrometer. Mass spectra were obtained on an LKB 9000 spectrometer. GLC analyses were performed on a column of 5% SE-30 on Chromosorb W. High-pressure liquid chromatography (HPLC) was performed on a Waters M-45 instrument with a μ-Porasil column (Silica, 10-μm packing, 0.4 × 30 cm). Melting points are uncorrected.

1,3-Cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, butadiene, isoprene, and (*E,E*)- and (*E,Z*)-2,4-hexadiene were purchased from FLUKA AG and were distilled before use. MnO_2 (precipitated active) was purchased from Merck-Schuchardt. 1,3-cyclopentadiene was prepared by cracking dicyclopentadiene at 170 °C. 5-Carbomethoxy-1,3-cyclohexadiene was prepared according to Trost et al.[34,45g] 3,5-Cycloheptadienol was prepared according to Schuster et al.[46] 1,2-Dibromo-1-methylcyclohexane,[47] 1,2-dibromo-3-methylcyclohexane,[47] and 1,2-dibromo-4-methylcyclohexane were prepared by bromination of the corresponding methylcyclohexene according to a literature procedure.[48]

5-Methyl-1,3-cyclohexadiene. 1,2-Dibromo-4-methylcyclohexane was treated with sodium isopropoxide in triglyme according to the procedure described for 1,3-cyclohexadiene.[6a] The

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following modifications were made: (i) sodium isopropoxide was prepared from isopropyl alcohol and sodium and (ii) pentane was added to the distillate (mainly consisting of isopropyl alcohol and diene) before washing with water. The pentane phase was dried ($MgSO_4$) and evaporated by using a Vigreux column. Distillation of the residue using a Vigreux column afforded the diene in 60% yield: bp 102 °C (lit.[47a] bp 105–106 °C).

2-Methyl-1,3-cyclohexadiene was prepared from 1,2-dibromo-1-methylcyclohexane by using the same procedure. The diene was obtained in 60% yield contaminated with about 10% of 3-methylenecyclohexene. Fractional distillation afforded a product that was >95% pure: bp 107 °C (lit.[47b] bp 109 °C).

1-Methyl-1,3-cyclohexadiene was prepared from 1,2-dibromo-3-methylcyclohexane in 50% yield by using the same procedure. Also this diene was contaminated with about 10% of 3-methylenecyclohexene. Fractional distillation afforded a product that was >95% pure: bp 107 °C (lit.[47c] bp 110 °C).

6-Methoxy-1,3-cycloheptadiene. 3,5-Cycloheptadienol (3.14 g, 0.029 mol) in dry tetrahydrofuran (20 mL) was slowly added to a stirred suspension of sodium hydride (1.8 g of an 80% suspension on mineral oil, 0.06 mol) in dry tetrahydrofuran (20 mL). The mixture was stirred at room temperature for 1 h. Methyl iodide (6.07 g, 0.043 mol) was added and the mixture was stirred at 40 °C for 40 h. The reaction mixture was filtered and concentrated and the residue was Kügelrohr distilled (75 °C, 1 mm) to afford 2.50 g (71%) of a clear liquid: ^1H NMR ($CDCl_3$) δ 5.9–5.6 (m, 4 H), 3.62 (m, 1 H, CHO), 3.36 (s, 3 H, OMe), 2.7–2.3 (m, 4 H).

6-Acetoxy-1,3-cycloheptadiene. 3,5-Cycloheptadienol (3.03 g, 0.028 mol) and acetic anhydride (8.9 mL) were dissolved in triethylamine (32 mL) at room temperature. 4-(Dimethylamino)pyridine (DMAP) (0.84 g, 6.9 mmol) was added in portions and the mixture was stirred at room temperature for 3.5 h. Methanol (100 mL) was added under cooling and the resulting solution was allowed to stir for 1.5 h. The solution was concentrated to a small volume and ether (150 mL) was added. The ether phase was washed with saturated $NaHCO_3$ (3 × 50 mL) and dried ($MgSO_4$). Evaporation of the solvent and Kügelrohr distillation afforded 3.25 g (77%) of the product as a light yellow oil: ^1H NMR ($CDCl_3$) δ 5.9–5.6 (m, 4 H), 5.11 (m, 1 H, CHO), 2.55 (m, 4 H), 2.04 (s, 3 H, OAc).

***trans*-1,4-Diacetoxy-2-cyclohexene (4).** To a stirred solution of $Pd(OAc)_2$ (700 mg, 3.1 mmol), $LiOAc{\cdot}2H_2O$ (6.8 g, 66.6 mmol), and *p*-benzoquinone (1.91 g, 17.6 mmol) in acetic acid (100 mL) was added MnO_2 (6.52 g, 74.9 mmol) followed by 1,3-cyclohexadiene (5.0 g, 62.5 mmol) dissolved in pentane (200 mL). The reaction mixture, which separated into a pentane phase and an acetic acid phase, was moderately stirred at room temperature for 8 h. The pentane phase was separated and collected and the remaining acetic acid phase was diluted with saturated NaCl (100 mL) and extracted with pentane (2 × 100 mL) and pentane/ether (1:1) (3 × 100 mL). The combined extracts were washed with saturated NaCl (3 × 40 mL), water (3 × 10 mL), and finally with 2 M NaOH (3 × 30 mL). The organic phase was dried ($MgSO_4$) and evaporated to yield 11.51 g (93%) of crystalline 4 (>91% trans). Recrystallization from hexane gave 9.87 g (80%) of isomerically pure 4 (>99% trans): mp 49–50 °C; IR (KBr) 1730, 1375, 1238, 1030, 1010, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.89 (br s, 2 H, CH=CH), 5.32 (m, 2 H, CHO), 2.1 (m, 2 H, CH_e–CH_e), 2.06 (s, 6 H, OAc), 1.7 (m, 2 H, CH_a–CH_a).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12; O, 32.29. Found: C, 60.44, H, 7.01; O, 32.19.

***trans*-2-Cyclohexene-1,4-diol.** To a solution of diacetate 4 (5.0 g, 25 mmol) in methanol (120 mL) was added 30 mL of aqueous 2 M NaOH. The mixture was heated to reflux for 15 min, cooled, and concentrated in vacuo to approximately 20 mL. The aqueous solution was saturated with NaOH (pellets) and extracted with ethyl acetate (6 × 25 mL). The organic phase was filtered through cotton to remove suspended water and then dried (Na_2SO_4). Evaporation of the solvent gave 2.76 g (97%) of pure *trans*-2-cyclohexene-1,4-diol as crystals: mp 83–84 °C; IR (KBr) 3260, 2920, 1445 cm^{-1}; ^1H NMR (aceton-d_6) δ 5.66 (s, 2 H, CH=CH), 4.14 (m, 2 H, CHO), 3.84 (d, 2 H, OH), 2.0 (m, 2 H, CH_e–CH_e), 1.43 (m, 2 H, CH_a–CH_a).

***cis*-1,4-Diacetoxy-2-cyclohexene (3).** Essentially the same procedure as for the preparation of 4 was used, but catalytic amounts of LiCl were added. To a stirred solution of $Pd(OAc)_2$ (700 mg, 3.1 mmol), LiCl (521 mg, 12, 3 mmol), $LiOAc{\cdot}2H_2O$ (21.5 g, 211 mmol), and *p*-benzoquinone (1.6 g, 14.8 mmol) in acetic acid (100 mL) was added MnO_2 (6.8 g, 78 mmol) followed by 1,3-cyclohexadiene (5 g, 62.5 mmol) in pentane (200 mL). After 22 h the same workup procedure as used for 4 gave 10.6 g (86%) of essentially pure *cis*-1,4-diacetoxy-2-cyclohexene (3) (>96% cis). Distillation afforded 9.8 g (79%): IR (neat) 2940, 1730, 1670, 1435, 1365, 1230, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (br s, 2 H, CH=CH), 5.23 (m, 2 H, CHO), 2.07 (s, 6 H, OAc) 1.9 (m, 4 H, CH_2–CH_2). Further characterization was obtained by hydrolysis to the known[8c] diol.

***cis*-2-Cyclohexene-1,4-diol.** The same hydrolysis as above gave 2.70 g (95% yield) of pure diol: mp 57–59 °C (lit.[8c] mp 57–59 °C).

***cis*-1,4-Diacetoxy-2-cycloheptene.** The same procedure as for the preparation of 3 was used but with only 2 equiv of LiCl per palladium and in a one-phase system. 1,3-Cycloheptadiene (0.564 g, 670 μL, 6 mmol), $Pd(OAc)_2$ (67.2 mg, 0.3 mmol), LiCl (25, 4 mg, 0.6 mmol), $LiOAc{\cdot}2H_2O$ (2.04 g, 20 mmol), *p*-benzoquinone (195 mg, 1.8 mmol), and MnO_2 (0.58 g, 6.7 mmol) in acetic acid (10 mL) were stirred at 40 °C for 36 h and gave after the usual workup 0.89 g (70%) of pure crystalline product (>99% cis). Recrystallization from hexane gave white crystals: mp 79–80 °C; IR (KBr) 1740, 1378, 1255, 1232, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (br s, 2 H, CH=CH), 5.37 (br d, J = 10.3 Hz, 2 H, CHO), 2.06 (s, 6 H, OAc), 2.1–1.6 (m, 6 H, CH_2); MS, *m/e* (relative intensity) 212 (M^+, 0.2), 152 (3), 153 (4), 127 (2), 110 (100), 95 (7), 93 (6), 92 (9), 91 (8), 82 (7), 81 (9).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60; O, 30.15. Found: C, 62.30; H, 7.52; O, 30.17.

In an alternative procedure LiCl is omitted which leads to a more rapid reaction. Reaction for 24 h at room temperature gave 1.08 g (85%) of crystalline *cis*-1,4-diacetoxy-2-cycloheptene (>95% cis).

***trans*-1,4-Diacetoxy-2-cycloheptene** was obtained in a mixture with the cis isomer by using a similar procedure without any lithium salts. 1,3-Cycloheptadiene (71 mg, 84 μL, 0.75 mmol), $Pd(OAc)_2$ (16.8 mg, 0.075 mmol), and *p*-benzoquinone (162 mg, 1.5 mmol) in acetic acid (2.5 mL) (18 h, 40 °C) gave after workup and Kügelrohr distillation 108 mg (68%) of a 66:34 mixture of *trans*- and *cis*-1,4-diacetoxy-2-cycloheptene. The isomers were separated by HPLC (hexane:ethyl acetate = 95:5) to give a pure sample of the trans isomer: IR (CCl_4) 2930, 1720, 1370, 1240, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.77 (br s, 2 H, CH=CH), 5.42 (m, w_H = 10 Hz, 2 H, CHO), 2.06 (s, 6 H, OAc), 1.86 (br s, 6 H, $(CH_2)_3$).

***trans*-1,4-Diacetoxy-2-cyclooctene.** 1,3-Cyclooctadiene (216 mg, 2 mmol), $Pd(OAc)_2$ (36 mg, 0.16 mmol), $LiOAc{\cdot}2H_2O$ (1.43 g, 14 mmol), and *p*-benzoquinone (435 mg, 4 mmol) were stirred in acetic acid (7 ml) at 35 °C for 17 h. The usual workup gave 254 mg (56%) of a light yellow oil consisting of 1,2-diacetoxy-3-cyclooctene, *trans*-1,4-diacetoxy-2-cyclooctene, and *cis*-1,4-diacetoxy-2-cyclooctene in a ratio of 1:9:1. The pure trans isomer was obtained by separation with HPLC (hexane:ethyl acetate = 90:10): IR (CCl_4) 2930, 2860, 1735, 1365, 1240, 1025; ^1H NMR ($CDCl_3$) δ 5.72 (m, 2 H, CHO), 5.62 (m, 2 H, CH=CH), 2.08 (s, 6 H, AcO), 1.87–1.70 (m, 6 H), 1.60–1.50 (m, 2 H). Further characterization of the diacetate was obtained by hydrolysis to the known *trans*-2-cyclooctene-1,4-diol.[49,50]

***cis*-1,4-Diacetoxy-2-cyclooctene.** 1,3-Cyclooctadiene (324 mg, 375 μL, 3 mmol), $Pd(OAc)_2$ (53, 9 mg, 0.24 mmol), and *p*-benzoquinone (648 mg, 6 mmol) were stirred in acetic acid (10 mL) at 40 °C for 24 h. The usual workup gave 390 mg (58%) of a light yellow oil consisting of 1,2-diacetoxy-3-cyclooctene, *trans*-1,4-diacetoxy-2-cyclooctene, and *cis*-1,4-diacetoxy-2-cyclooctene in a ratio of 1:2:10. The pure cis isomer was obtained by separation with HPLC (hexane:ethyl acetate = 90:10). An es-

(49) The *cis*- and *trans*-2-cyclooctene-1,4-diols have been described and characterized by Barrelle and Apparu.[50a] However, the authors did not assign the stereochemistry of these isomers, which melt at 106 °C and 154 °C. From later work by Horinaka et al., it is evident that the high melting isomer is the cis isomer.[50b]

(50) (a) Barrele, M.; Apparu, M. *Bull. Soc. Chim. Fr.* **1972**, 2016. (b) Horinaka, A.; Nakashima, R.; Yoshikawa, M.; Matsuura, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2095.

sentially pure sample of the cis isomer can be obtained in a reasonable yield (30%) on a preparative scale by flash chromatography (silica, hexane:ethyl acetate = 80:20): IR (CCl_4) 2930, 2860, 1735, 1365, 1235, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.58 (m, 2 H, CHO), 5.56 (m, 2 H, CH=CH) 2.04 (s, 3 H, AcO), 2.05–1.90 (m, 2 H), 1.6 (m, 6 H).

Further characterization of the cis diacetate was obtained by hydrolysis to the known[49,50] *cis*-2-cyclooctene-1,4-diol by using the procedure described above (97% yield). The diol obtained was recrystallized from ethyl acetate: mp 154–56 °C (lit.[49,50] mp 154 °C, 143–151 °C).

***cis*-1,4-Diacetoxy-2-cyclopentene.** Cyclopentadiene (310 mg, 4.7 mmol), $Pd(OAc)_2$ (84 mg, 0.38 mmol), $LiOAc{\cdot}2H_2O$ (6.06 g, 59 mmol), LiCl (1.47 g, 35 mmol), MnO_2 (750 mg, 8.6 mmol), and *p*-benzoquinone (70 mg) were stirred in acetic acid (12.5 mL)–water (20.5 mL)–pentane (180 mL) at 20 °C for 72 h. The usual workup afforded 350 mg (40%) of *cis*-1,4-diacetoxy-2-cyclopentene (>98% cis) that was identified by its spectral data.[8c]

***trans*-1,4-Diacetoxy-2-methyl-2-cyclohexene.** Diacetoxylation of 2-methyl-1,3-cyclohexadiene according to the procedure used for preparation of **4**: yield 71% (>95% trans) contaminated with 20% of the 1,2-isomer; IR (neat) 2940, 1725, 1370, 1240, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.69 (br s, 1 H, CH=C), 5.27 (m, 2 H, CHO), 2.08 (s, 3 H, AcO), 2.05 (s, 3 H, AcO), 2.2–1.65 (m, 4 H, CH_2–CH_2), 1.72 (br s, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.26; H, 7.50.

***cis*-1,4-Diacetoxy-2-methyl-2-cyclohexene**: diacetoxylation of 2-methyl-1,3-cyclohexadiene according to the procedure used for preparation of **3** except that only 12 mol % of *p*-benzoquinone was used; yield 51% (>95% cis); IR (neat) 2940, 1735, 1650, 1370, 1235, 1030, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (br s, 1 H, CH=C), 5.20 (m, 2 H, CHO), 2.08 (s, 3 H, OAc), 2.06 (s, 3 H, OAc) 1.93–1.81 (m, 4 H, CH_2–CH_2), 1.71 (br s, 3 H, CH_3).

***trans*-1,4-Diacetoxy-1-methyl-2-cyclohexene**: diacetoxylation of 1-methyl-1,3-cyclohexadiene according to the procedure used for preparation of **4**: yield 70% (>95% trans); IR (neat) 2940, 1735, 1675, 1370, 1240, 1200, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.27, (d, J = 10 Hz, 1 H, CH=C), 5.79 (dd, J = 10 Hz and 5 Hz, 1 H, CH=C), 5.27 (m, w_H = 8 Hz, 1 H, CHO), 2.05 (s, 3 H, AcO), 1.97 (s, 3 H, AcO), 2.2–1.65 (m, 4 H, CH_2CH_2), 1.58 (s, 3 H, CH_3).

1,4-Diacetoxy-5-methyl-2-cyclohexene (8 and 9). The procedure for cis diacetoxylation was used (cf. preparation of **3**) but only 15 mol % of *p*-benzoquinone was used. 5-Methyl-1,3-cyclohexadiene (109 mg, 1.16 mmol) gave after 43 h reaction and the usual workup 170 mg (69%) of a 58:42 mixture of **8** and **9** as determined by ^1H NMR (contains <5% of **10** and **11**). The mixture was separated by HPLC (hexane:ethyl acetate = 95:5) to give pure samples of each isomer.

1β,4β-Diacetoxy-5β-methyl-2-cyclohexene (8): IR (CCl_4) 2930, 1710, 1360, 1220, 1090, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.97 (ddd, J = 10 Hz, 5 Hz, and 2 Hz, 1 H, CH=C), 5.86 (dt, J = 10 Hz and 1.5 Hz, 1 H, CH=C), 5.32 (m, w_H = 20 Hz, 1 H, CHO), 5.14 (br t, $J_{av} \approx$ 4 Hz, 1 H, CHO), 2.07 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.03–1.65 (m, 3 H, $CHCH_2$), 0.98 (d, 3 H, CH_3).

1β,4β-Diacetoxy-5α-methyl-2-cyclohexene (9): IR (CCl_4) 2930, 1725, 1370, 1240, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (br s, 2 H, CH=CH), 5.24 (br q, $J_{av} \approx$ 4 Hz, 1 H, CHO), 4.98 (br d, J = 9 Hz, 1 H, CHO), 2.09 (s, 3 H, OAc), 2.06 (s, 3 H, AcO), 2.2–1.65 (m, 3 H, $CHCH_2$), 0.99 (d, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{16}O_4$ (isomer mixture): C, 62.25; H, 7.60. Found: C, 61.83; H, 7.42.

1,4-Diacetoxy-5-methyl-2-cyclohexene (10 and 11). The usual procedure for trans diacetoxylation was used (cf. preparation of **4**). 5-Methyl-1,3-cyclohexadiene (0.70 g, 7.4 mmol) gave after 13 h and the usual workup 1.29 g (82%) of a 3:1 mixture between **10** and **11** contaminated with 9% of **9**. The mixture was separated by HPLC (hexane:ethyl acetate = 95:5) to give pure samples of each isomer.

1α,4β-Diacetoxy-5β-methyl-2-cyclohexene (10): IR (CCl_4) 2920, 1720, 1365, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.00 (m, 2 H, CH=CH), 5.29 (br q, J = 4 Hz and 3.9 Hz, 1 H, CHO), 5.21 (br t, J = 4 Hz and 3.9 Hz, 1 H, CHO), 2.21 (m, 1 H, $CHCH_3$) 2.06 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.87 (m, 1 H), 1.69 (m, 1 H), 0.98 (d, 3 H, CH_3).

1α,4β-Diacetoxy-5α-methyl-2-cyclohexene (11): IR (CCl_4) 2920, 1710, 1360, 1220, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.73 (br s, 2 H, CH=CH), 5.42 (m, w_H = 20 Hz, 1 H, CHO), 5.10 (dd, J = 9 Hz and 3 Hz, 1 H, CHO), 2.09 (s, 3 H, OAc), 2.06 (s, 3 H, AcO), 2.25–1.7 (m, 3 H, $CHCH_2$), 1.01 (d, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{16}O_4$ (isomer mixture): C, 62.25; H, 7.60. Found: C, 62.51; H, 7.63.

1β,4β-Diacetoxy-5β-carbomethoxy-2-cyclohexene (13). The procedure for cis diacetoxylation was used but 200 mol % of *p*-benzoquinone was used as the oxidant (without MnO_2). Reaction for 45 h followed by the usual workup gave 59% yield of **13** contaminated with $^1/_{10}$ of the 1β,4β,5α isomer. An isomerically pure sample of **13** was obtained by HPLC separation (hexane:ethyl acetate 92:8): IR (CCl_4) 2930, 1725, 1370, 1240, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.05 (ddd, J = 11, 4.6, and 1.8 Hz, 1 H, CH=C), 5.74 (dt, J = 11, 1.8, and 1.5 Hz, 1 H, CH=C), 5.53 (br t, J = 3.8 and 4.6 Hz, 1 H, CHO), 5.36 (m, w_H = 25 Hz, 1 H, CHO), 3.70 (s, 3 H, OMe), 2.81 (dt, J = 13.7 and 3.5 Hz, 1 H, CHCOO), 2.37 (m, 1 H), 2.09 (s, 3 H, OAc) 2.01 (s, 3 H, OAc), 1.97 (m, 1 H).

Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 56.39; H, 6.77.

A pure sample of the minor stereoisomer **1β,4β-diacetoxy-5α-carbomethoxy-2-cyclohexane** was obtained from the HPLC separation: IR (neat) 1735, 1370, 1235, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.90 (m, 2 H, CH=CH), 5.61 (br d, J = 9 Hz, 1 H, CHO) 5.27 (br q, $J_{av} \approx$ 4 Hz, 1 H, CHO) 3.72 (s, 3 H, CH_3O), 2.97 (ddd, J = 11.5, 9, and 4.5 Hz, 1 H, CHCOO), 2.07 (s, 6 H, AcO), 2.35–1.90 (m, 2 H, CH_2).

1β,4β-Diacetoxy-6α-methoxy-2-cycloheptene (6b). 6-Methoxy-1,3-cycloheptadiene (186 mg, 1.5 mmol), $Pd(OAc)_2$ (16.8 mg, 0.075 mmol), $LiOAc{\cdot}2H_2O$ (765 mg, 7.5 mmol), MnO_2 (150 mg, 1.7 mmol), and *p*-benzoquinone (32 mg, 0.30 mmol) were stirred in acetic acid (2.5 mL) at 30 °C for 36 h. The usual workup afforded 326 mg (89%) of **6b**: IR (neat) 2935, 1740, 1440, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.69 (s, 2 H, CH=CH), 5.67 (br d, 2 H, CHOAc), 3.72 (m, 1 H, CHOMe) 3.43 (s, 3 H, OMe), 2.17 (ddd, 2 H, CH_2), 2.06 (s, 6 H, OAc), 1.85 (ddd, 2 H, CH_2).

Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.38; H, 7.31.

From the ^1H NMR analysis none of the other possible diastereoisomers could be detected. HPLC and GLC gave one single peak.

1α,4β-Diacetoxy-6α-methoxy-2-cycloheptene was obtained in a 1:2 mixture (minor component) with **6b** by using the salt free procedure described for preparation of *trans*-1,4-diacetoxy-2-cycloheptene: IR (CCl_4) 2920, 1730, 1240, 1090, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75 (br s, 2 H, CH=CH), 5.51 (m, 1 H, CHOAc), 5.40 (br d, 1 H, CHOAc), 3.73 (m, 1 H, CHOMe), 3.35 (s, 3 H, OMe), 2.33 (dd, 1 H, CH), 2.08 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.1-1.9 (m, 2 H), 1.77 (m, 1 H, CH).

1β,4β,6α-Triacetoxy-2-cycloheptene (6a). The same procedure as described for preparation of **6b** was used. 6-Acetoxy-1,3-cyclohexadiene (228 mg, 1.5 mmol) gave after 72 h 315 mg (78%) of **6a**: IR (CCl_4) 2920, 1740, 1430, 1365, 1230, 1070, 1020, 905 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.76 (br s, 2 H, CH=CH), 5.67 (br dd, 2 H, CHOAc), 5.31 (m, 1 H, CHOAc), 2.1–1.9 (m, 4 H, two CH_2), 2.13 (s, 3 H, OAc), 2.02 (s, 6 H, OAc).

The use of Li_2PdCl_4 as catalyst (8 mol %) and *p*-benzoquinone (1.9 equiv to the diene) as oxidant gave 73% yield of **6a**.

***(E)-meso*-2,5-Diacetoxy-3-hexene (18).** (*E*,*Z*)-2,4-Hexadiene (574 mg, 7 mmol), $Pd(OAc)_2$ (125 mg, 0.56 mmol), $LiOAc{\cdot}2H_2O$ (5.36 g, 52.5 mmol), LiCl (71 mg, 1.68 mmol), and *p*-benzoquinone (1.51 g, 14 mmol) were stirred in acetic acid (21 mL) at 35 °C for 48 h. The ususal workup afforded 716 mg (51%) of the diacetate **18** (>95% meso and >99% *E*), which was shown by subsequent experiments to be the meso isomer (see below): IR (CCl_4) 2970, 2920, 1730, 1650, 1445, 1365, 1230, 1040, 950 (*trans*-CH=CH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.70 (dd, 2 H, CH=CH), 5.35 (m, 2 H, CHO), 2.05 (s, 6, OAc), 1.30 (d, J = 6.5 Hz, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 170.02 (C=O), 131.18 (C=C), 69.94 (CHO), 21.25 (CH_3), 20.09 (CH_3). The *dl*:meso ratio was determined from the ^{13}C NMR spectrum (olefin carbon signals of dl and meso separates). The *E* purity was established by HPLC, by comparison with an authentic sample of the *Z* isomer.[16a]

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; Found: C, 60.15; H, 8.03.

(*E*)-*dl*-2,5-Diacetoxy-3-hexene (15). (*E,E*)-2,4-Hexadiene (410 mg, 5 mmol), $Pd(OAc)_2$ (125 mg, 0.56 mmol), $LiOAc{\cdot}2H_2O$ (3.06 g, 30 mmol), MnO_2 (478 mg, 5.5 mmol), and *p*-benzoquinone (108 mg, 1 mmol) were stirred in acetic acid (13.5 mL)–water (1.5 mL)–hexane (15 mL) at 35 °C for 72 h. The usual workup gave 691 mg of crude product, which on Kügelrohr distillation afforded 405 mg (40%) of **15** (*dl*:meso = 88:12, and >99% *E*). Subsequent experiments showed that the diacetate was mainly *dl*: IR (CCl_4) 2970, 2920, 1770, 1445, 1370, 1230, 1040, 950 (*trans*-CH=CH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.70 (dd, 2 H, CH=CH), 5.35 (m, 2 H, CHO), 2.05 (s, 6 H, OAc), 1.30 (d, J = 6.3 Hz, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 170.13 (C=O), 131.10 (C=C), 69.94 (CHO), 21.29 (CH_3), 20.13 (CH_3). The *dl*:meso ratio was determined from the ^{13}C NMR spectrum (olefin carbon signals of *dl* and meso separates). The *E* purity was established by HPLC.

Stereochemical Assignment of *dl*- and *meso*-2,5-Diacetoxy-3-hexenes 15 and 18. The diacetate (**15** or **18**) was hydrolyzed to the corresponding diol utilizing the hydrolysis procedure used above. The diols were isolated in a yield between 90–95%. The diols (meso or *dl*) showed very similar ^1H NMR spectra: ^1H NMR ($CDCl_3$) δ 5.74 (dd, 2 H, CH=CH), 4.32 (m, 2 H, CHO), 1.8 (br s, 2 H, OH), 1.28 (d, J = 6.4, 6 H, CH_3).

(*E*)-3-Hexene-2,5-diol (373 mg, 3.21 mmol), PtO_2 (29 mg, 0.128 mmol), and methanol (12 mL) together with a magnetic stirrer bar were placed in a glass autoclave. The autoclave was flushed with nitrogen and then with hydrogen. The hydrogen pressure was adjusted to a gauche pressure of 4.1 kg/cm^2. After stirring for 1 h and 10 min at room temperature the solution was filtered and concentrated in vacuo. Kügelrohr distillation afforded 346 mg (91%) of the diol.[33] The meso and *dl* diols **16** and **19** have slightly different ^1H NMR spectra but not enough to allow a quantitative analysis. **16** (*dl* isomer): ^1H NMR ($CDCl_3$) δ 3.825 (m, 2 H, CHO), 2.55 (m, 4 H, CH_2CH_2), 1.20 (d, J = 6.2 Hz, 6 H, CH_3). **19** (meso isomer): ^1H NMR ($CDCl_3$) δ 3.855 (m, 2 H, CHO), 2.5 (m, 4 H, CH_2CH_2), 1.21 (d, J = 6.2 Hz, 6 H, CH_3).

The diol was treated with 25% H_2SO_4 at 110 °C according to the procedure described by Mihailovic et al.[27] The reaction proceeds with inversion at one center and gives the corresponding 2,5-dimethyltetrahydrofuran. The cis/trans ratio of the 2,5-dimethyltetrahydrofuran was determined from its ^1H NMR spectrum at 200 MHz by integration over the CHO protons. The CHO protons appear at δ = 4.14 ppm for the trans compound and at 3.93 ppm for the cis compound ($CDCl_3$).[51]

(*E*)-2,5-Diacetoxy-3-hexene. Mixture of *dl* and meso (15 and 18). (*E,Z*)-2,4-hexadiene (574 mg, 7 mmol), $Pd(OAc)_2$ (125 mg, m 0.56 mmol), $LiOAc{\cdot}2H_2O$ (3.21 g, 31.5 mmol), and *p*-benzoquinone (1.51 g, 14 mmol) were stirred in acetic acid (21 mL) at 35 °C for 40 h. The usual workup gave 1.40 g (100%) of crude product which on Kügelrohr distillation afforded 1.25 g (89%) of a 60:40 *dl*:meso mixture of *E*-2,5-diacetoxy-3-hexene. The *dl*:meso ratio was determined as described above.

1,4-Diacetoxy-2-methyl-2-butene. Isoprene (102 mg (150 μL), 1.5 mmol) was added in five portions over 8 h to a slowly stirred solution of $Pd(OAc)_2$ (25.2 mg, 0.1125 mmol), $LiOAc{\cdot}2H_2O$ (1.22 g, 12 mmol), and *p*-benzoquinone (330 mg, 3 mmol) in acetic acid (5 mL)–pentane (8 mL) at room temperature. The mixture was slowly stirred for 30 h. The usual extractive workup afforded 175 mg of crude product of a mixture of diacetate and Diels–Alder adduct. The crude product was dissolved in 20 mL of pentane–ether (90:10) and treated with $NaBH_4$ (20 mg, 0.5 mmol) in 3 mL of 1 M NaOH. The mixture was stirred for 30 min, and the organic phase was collected and evaporated. Kügelrohr distillation afforded 83 mg (30%) of a 1,4-diacetoxy-2-methyl-2-butene (*E/Z* = 5.5:1) that was >90% 1,4-isomer.

The products were identified with the reported spectra of the known compounds. However, the tentative assignment of the *E* and *Z* isomers previously reported[4b] is the reversed one. For clarity we therefore give the ^1H NMR spectrum of our product.

(*E*)-1,4-Diacetoxy-2-methyl-2-butene: ^1H NMR δ ($CDCl_3$) 5.62 (t with q splittings, J = 7 Hz, 1.3 Hz, 1 H, =CH), 4.64 (d, J = 6.9 Hz, 2 H, CH_2O), 4.50 (br s, 2 H, CH_2O), 2.10 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 1.74 (br s, 3 H, CH_2O), 2.10 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 1.74 (br s, 3 H, CH_3). The *Z* isomer is distinguishable in an *E/Z* mixture by ^1H NMR ($CDCl_3$) δ 1.82 (br s, CH_3). Also the singlet for the CH_2O protons is different and appears at δ 4.63 for the *Z* isomer.

The assignment is based on the comparison with the known *E* and *Z* isomers of 1-acetoxy-4-chloro-3-methyl-2-butene where the methyl group on the double bond in the *Z* isomer appears at lower field by 0.07 ppm (^1H NMR).[52,53] Also, in analogy with the palladium-catalyzed acetoxychlorination reaction,[15d,53] the expected major product in the present diacetoxylation reaction is the *E* isomer.

1,4-Diacetoxy-2-butene. Diacetoxylation of 1,3-butadiene was performed as for isoprene (on a 6-mmol scale) except that all butadiene was added in the beginning of the reaction: yield 49% of a 3:1 mixture of 1,4-diacetoxy-2-butene (*E/Z* = 94:6) and 1,2-diacetoxy-2-butene.[4] The *Z* isomer prepared by acetylation of (*Z*)-2-butene-1,4-diol differs from the *E* isomer in the ^1H NMR spectrum: $(\delta_{CH_2})_Z$ = 4.69 ppm, $(\delta_{CH_2})_E$ = 4.59 ppm ($CDCl_3$).

1,4-Diacetoxy-2-pentene: IR (CCl_4) 2960, 2920, 1740, 1660, 1430, 1365, 1230, 1020, 965 (*trans*-CH=CH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (m, 2 H, CH=CH), 5.37 (m, 1 H, CHO), 4.56 (m, 2 H, CHO), 2.075 (s, 3 H, OAc) 2.052 (s, 3 H, OAc), 1.32 (d, 3 H, CH_3).

Stereochemical Assignment of Cyclic Diacetates. The assignment of the diacetates from 1,3-cyclohexadiene and 1,3-cycloheptadiene was made in a preliminary communication[15c] and has been confirmed by chemical transformations. The ^1H NMR spectra of 1,4-diacetoxy-2-cyclohexenes are characteristic in that the $-CH_2CH_2-$ protons of the flexible cis isomer appear at 1.9 ppm, whereas the $-CH_2CH_2-$ protons of the more or less locked trans isomer appear at 2.1 and 1.7 ppm. Furthermore, the allylic protons (*CH*OAc) appear at lower field in the trans isomer.

cis- and *trans*-1,4-diacetoxy-2-methyl-2-cyclohexene were assigned in the same manner. For the $-CH_2CH_2-$ protons the δ values (^1H NMR) are concentrated at 1.9 for the cis isomer but appear at δ 2.1 and 1.7 for the trans isomer.

For *trans*-1,4-diacetoxy-1-methyl-2-cyclohexene the assignment follows from the width at half height (w_H) of the CHOAc proton, which is 8 Hz for this isomer. The w_H value for the cis isomer is 12 Hz. This is consistent with chair conformations in which the methyl group is equatorial.

The assignment of the 1,4-diacetoxy-5-methyl-2-cyclohexenes **8–11** is based on the fact that the methyl group has a much higher standard free energy change for the equatorial/axial equilibrium than the acetate.[24] The methyl group will therefore preferentially possess an equatorial position in all the isomers **8–11**. They can therefore be assigned from their ^1H NMR data given above (coupling constants and/or w_H).

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Registry No. **3**, 78776-45-1; **4**, 78776-44-0; **5a**, 29207-42-9; **5b**, 54561-42-1; **6a**, 92008-76-9; **6b**, 92490-02-3; **7**, 19656-98-5; **8**, 92489-98-0; **9**, 92489-97-9; **10**, 92489-99-1; 11, 92490-00-1; **13**, 20065-92-3; **15**, 92490-05-6; **16**, 38484-56-9; 18, 92490-04-5; **19**, 38484-55-8; MnO_2, 1313-13-9; LiOAc, 546-89-4; LiCl, 7447-41-8; 1,3-cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 2-methyl-1,3-cyclohexadiene, 1489-57-2; 1-methyl-1,3-cyclohexadiene, 1489-56-1; methyl 2,4-cyclohexadiene-1-carboxylate, 54162-19-5; 1,3-cyclooctadiene, 1700-10-3; 1,3-butadiene, 106-99-0; 2-methyl-1,3-butadiene, 78-79-5; palladium acetate, 3375-31-3; *p*-benzoquinone, 106-51-4; *trans*-2-cyclohexene-1,4-diol, 41513-32-0; *cis*-2-cyclohexene-1,4-diol, 53762-85-9: *cis*-1,4-diacetoxy-2-cycloheptene, 92489-91-3; *trans*-1,4-diacetoxy-2-cycloheptene, 92489-92-4; *trans*-1,4-diacetoxy-2-cyclooctene, 92489-93-5; *cis*-1,4-diacetoxy-2-cyclooctene, 92489-94-6; *cis*-1,4-diacetoxy-2-

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(52) It seems to be a general phenomenon that the methyl group in a (*Z*)-trisubstituted olefin appears at lower field by 0.07–0.09 ppm compared to the *E* isomer. For example, see: Bowlus, S. B.; Katzenellenbogen, J. A. *J. Org. Chem.* **1973**, *38*, 2733. Cooke, M. P., Jr. *Tetrahedron Lett.* **1973**, 1281.

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cyclopentene, 54664-61-8; *trans*-1,4-diacetoxy-2-methyl-2-cyclohexene, 92489-95-7; *cis*-1,4-diacetoxy-2-methyl-2-cyclohexene, 59055-07-1; *trans*-1,4-diacetoxy-1-methyl-2-cyclohexene, 92489-96-8; 1β,4β-diacetoxy-5α-carbomethoxy-2-cyclohexene, 92490-01-2; 1α,4β-diacetoxy-6α-methoxy-2-cycloheptene, 92490-03-4; (*Z*)-1,4-diacetoxy-2-methyl-2-butene, 59055-00-4; (*E*)-1,4-diacetoxy-2-methyl-2-butene, 59054-99-8; (*E*)-1,4-diacetoxy-2-butene, 1576-98-3; (*E*)-1,4-diacetoxy-2-pentene, 92490-06-7; 2(*E*),4(*E*)-hexadiene, 5194-51-4; 2(*E*),4(*Z*)-hexadiene, 5194-50-3; (*E*)-1,3-pentadiene, 2004-70-8; (*Z*)-1,4-diacetoxy-2-butene, 25260-60-0.

Kinetic Control and Locoselectivity in the Electrophilic Cleavage of Allylic Aluminum Compounds: Reactions of Acenaphthenylaluminum Reagents with Carbonyl Substrates[1]

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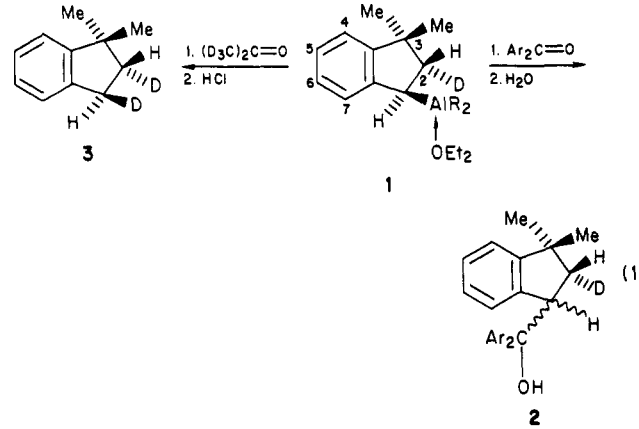
The benzylic reagent 1-acenaphthenyldiisobutylaluminum, which is formed by the addition of diisobutylaluminum hydride to acenaphthylene, exhibits a ^1H NMR spectrum at 25 °C consistent with a C_1–Al bond. At 110 °C the carbon–aluminum bond undergoes configurational inversion, as evidenced by the magnetic equivalence of the cis and trans C_2 protons. At −78 °C this aluminum compound reacts with ketones to give, upon hydrolysis, 65–75% of 3-(α-hydroxy-disubstituted methyl)-1,3-dihydroacenaphthylenes, which undergo acid-catalyzed isomerization to 3-(α-hydroxy-disubstituted methyl)acenaphthenes and which dissociate into acenaphthene and the ketone upon contact with Pd. On the other hand, the same reagents at 80–100 °C lead to the formation of 75–85% of 1-(α-hydroxy-disubstituted methyl)acenaphthenes. Similar reactions with acyl chlorides (RCOCl, where R = Me, Et, Ph) and with Me_3SiCl lead to 3-acylacenaphthenes and 1-(trimethylsilyl)acenaphthene, respectively. The stereochemically defined adduct of acenaphthylene and diisobutylaluminum deuteride, (*cis*-2-deuterio-1-acenaphthenyl)diisobutylaluminum diethyl etherate, is found to react with 9-fluorenone at 65 °C to yield a 1:1 mixture of *cis*- and *trans*-2-deuterio-1-acenaphthenylcarbinols. Similarly, treatment of the same aluminum reagent with O_2 gives a 1:1 mixture of *cis*- and *trans*-2-deuterio-1-acenaphthenols. The magnetically shielded C_8 or ortho proton in the original aluminum adduct offers a valuable monitor of the extent of complexation at the C_1–Al bond. The present findings demonstrate that electrophilic attack at the ortho position (leading to C_3 substitution) is the kinetically controlled process, while rearrangement to C_1 is thermodynamically determined.

The interaction of aluminum alkyls with carbonyl compounds raises an array of interesting mechanistic questions, since modest changes in the structure of the reactants or in experimental conditions can lead to varying amounts of 1,2-carbalumination,[2] conjugate or 1,4-carbalumination,[3] enol–salt formation,[4] or reduction by aluminum hydride transfer.[5] By employing aluminum alkyls having carbon–aluminum bonds of known configuration, previous work has provided stereochemical insight into two of these processes, namely, 1,2-carbalumination and enol–salt formation.[6] Thus, diisobutyl((1*R*,2*S*)-2-deuterio-3,3-dimethyl-1-indanyl)aluminum diethyl etherate[7] (1) was shown to insert the ketone 9-fluorenone with loss of configuration at the 1-indanyl position (2), but this aluminum reagent caused enolate formation with acetone with retention of configuration at the same indanyl site (3) (eq 1).



With benzylic aluminum compounds, such as 1, an additional reaction pathway with carbonyl substrates becomes competitive: orthoalkylation via allylic rearrangement. For example, the reaction of 1 with CO_2 leads principally to the indan-7-carboxylic acid.[8] In order to evaluate the factors determining the competition between normal 1,2-carbalumination and carbalumination with allylic rearrangement, therefore, we have examined the reactivity of 1-acenaphthenyldiisobutylaluminum (4) to-

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