mixture was kept overnight at 70 °C and worked up as described for **14** above. The orange oil obtained (0.45 g) was chromatographed on dry silica column (Woelm TSC) by using toluene as the eluant. Crystallization from EtOH gave 0.35 g (65%) of colorless crystals of isopropyl dimesitylacetate: mp 90 °C; UV (hexane) λ_{max} 207 nm (log ϵ = 4.56), 265 (2.89); IR (Nujol) ν_{max} 1725 (C=O), 1610 (C=C) cm^{-1}; ^1H NMR (CD_2Cl_2, room temperature) δ 1.16 (6 H, d, J = 6.3 Hz, 2Me), 1.95 (12 H, s, 4Me), 2.14 (6 H, s, 2Me), 4.98 (1 H, *m*, J = 6.3 Hz, CH), 5.18 (1 H, s, CH), 6.70 (4 H, s, Mes—H); mass spectrum, *m/z* 338 (M, 13%), 251 (Mes_2CH^+, 100%), 236 (Mes_2CH^+ - Me, 4%), 221 (Mes_2CH^+ - 2Me, 10%), 206 (Mes_2CH^+ - 3Me, 6%), 43 (C_3H_7, 8%). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.97; H, 9.05.

Equilibration Studies. Approximately 20 mg of the ketone or the enol was dissolved in 25 mL of spectroscopic hexane, and the solution was divided into several pressure ampules which were wrapped in aluminum foil and were kept in an oil bath in the dark at 80.3 ± 0.1 °C. If the ampules of the enols were kept at daylight, decomposition took place as reflected by the appearance of new (non-ketonic) signals in the NMR. For example, the reaction of **5** gave signals (in $CDCl_3$) at 0.99 (s), 2.19 (s), 4.7 (AB q), 6.6 (s), and 9.54 (s) ppm.

Samples were withdrawn after a few hours, the solvent was evaporated, and the ^1H NMR spectra in $CDCl_3$ were recorded. The relative ratios of the two species were determined by integration of the methyls of the alkyl groups for each one of the keto/enol pairs. In several cases, a corroboration for this ratio was obtained from the integration of the ketonic CH and enolic OH protons, but this was impossible when traces of CF_3COOH still remained, since exchange with the OH resulted in a higher integration. Care was taken to ensure complete relaxation of the various hydrogens in order to obtain reliable integration. When two or three samples taken at different reaction times gave a similar enol/ketone composition, this was regarded as the equilibrium value. In all cases, the equilibrium compositions obtained by starting from the enol or from the ketone were identical within the accuracy of the integration.

Acknowledgment. We are indebted to Silvio Biali for discussions and for some experiments with **13** and **14**, to Prof. H. Schwarz for the mass spectra of **14**, to Dr. S. Cohen for the X-ray crystallography of compound **14**, and to Dr. L. Radom for discussions. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

Registry No. 1, 54288-04-9; **2**, 89959-15-9; **3**, 96040-90-3; **4**, 96040-91-4; **5**, 89959-16-0; **6**, 94203-58-4; **7**, 96040-92-5; **8**, 96040-93-6; **9**, 96040-94-7; **10**, 96040-95-8; **11**, 87871-33-8; **12**, 96040-98-1; **13**, 96040-97-0; **14**, 96040-96-9; dimesitylacetic acid, 5740-42-1; isopropyl bromide, 75-26-3; *tert*-butyl bromide, 507-19-7; ethyl bromide, 74-96-4.

Supplementary Material Available: Tables S1–S4 giving the crystallographic data for compound **14** (6 pages). Ordering information is given on any current masthead page.

Stereo- and Regioselective Palladium-Catalyzed, 1,4-Acetoxychlorination of 1,3-Dienes. 1-Acetoxy-4-chloro-2-alkenes as Versatile Synthons in Organic Transformations

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Abstract: Palladium-catalyzed oxidation of 1,3-dienes in the presence of LiCl and LiOAc produces 1-acetoxy-4-chloro-2-alkenes with high selectivity. The reaction is stereospecific and cyclic dienes give an overall cis 1,4-addition (>97–98% cis). The stereospecificity of the reaction also holds in acyclic systems as shown by the oxidation of (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene to (*R**,*R**)- and (*R**,*S**)-**10**, respectively. The mechanism of the acetoxychlorination is now well understood. It proceeds via a trans acetoxypalladation of the diene to produce an intermediate (4-acetoxy-1,2,3-η^3-allyl)palladium species, followed by an oxidation-induced nucleophilic attack at C-1 with inversion. Kinetic studies indicate that *p*-benzoquinone, which is a unique oxidant for the reaction, not only serves as an oxidant but also acts as a ligand to palladium. The chloroacetate products are useful synthons in organic transformations. Sequential substitutions of the chloro and acetoxy groups allow a *regiochemical choice*, and the fact that the allylic chloro group can be substituted with either clean retention or inversion allows a *stereochemical choice*. These principles are demonstrated in a number of cases. It is shown that the acetoxychlorination approach allows a *complete control* of the 1,4-relative stereochemistry with a unique choice of functionality at the asymmetric center.

Regio- and stereocontrolled 1,4-addition to conjugated dienes is of synthetic interest. Methods for achieving such additions include cycloaddition of singlet oxygen[1,2] and nitroso compounds[3,4] followed by reduction.[5] We recently reported a few stereo- and regioselective 1,4-additions to conjugated dienes.[6,7] These oxi-

(1) (a) Balci, M. *Chem. Rev.* **1981**, *81*, 91. (b) Schenck, G. O.; Dunlop, D. E. *Angew. Chem.* **1956**, *68*, 248.

(2) (a) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876. (b) Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1983**, *24*, 3303.

(3) (a) Belleau, B.; Au-Young, Y. K. *J. Am. Chem. Soc.* **1963**, *85*, 64. (b) Krezse, G.; Dittel, W.; Melzer, H. *Liebigs Ann. Chem.* **1981**, 224 and references cited. (c) Keck, G. E.; Fleming, S. A. *Tetrahedron Lett.* **1978**, 4763.

(4) (a)Streith, J.; Augelmann, G.; Fritz, H.; Strub, H. *Tetrahedron Lett.* **1982**, *23*, 1909. (b) Becker, Y.; Eisenstadt, A.; Shvo, Y. *Tetrahedron* **1978**, *34*, 801.

(5) 1,4-Additions to conjugated dienes have been obtained in a limited number of electrophilic and radical additions. Most of these reactions, however, are not general, and furthermore, the reactions are either not stereoselective or the stereochemistry of the additions is unknown: (a) Neale, R. S. *Synthesis* **1971**, 1. (b) Hassner, A.; Keogh, J. *Tetrahedron Lett.* **1975**, 1575. (c) Truce, W. E.; Goralski, C. T.; Christensen, L. W.; Bavry, R. M. *J. Org. Chem.* **1970**, *35*, 4217. (d) Adams, D. R.; Bhatuagar, S. P.; Cookson, R. C. *Tetrahedron Lett.* **1974**, 3197. (e) Matsumoto, H.; Nateaur, T.; Nikaido, T.; Nagai, Y. *Chem. Lett.* **1978**, 115.

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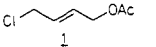
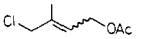
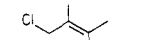
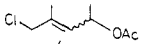
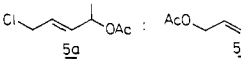
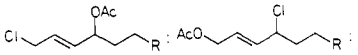
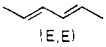
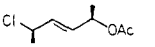
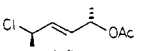
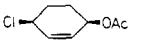
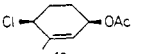
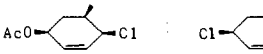
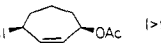
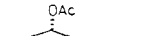
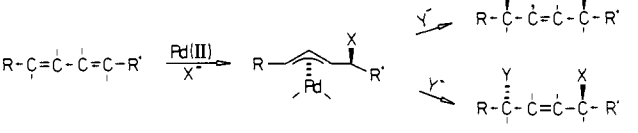
Table I. Palladium(II)-Catalyzed 1,4-Acetoxychlorination of Conjugated Dienes

Entry	Diene	Method[a], reaction time (addition time) h	Product(s)		Yield %
1a		A, 26 (0)	 1	(E/Z = 9/1)	81[b]
b		B, 20 (16)			78[b]
2a		A, 22 (0)	 2	(E/Z = 36/1)	76[c]
b		B, 26 (16)			74[c]
3a		A, 20 (0)			44[d]
b		B, 32 (28)	(Z)-3	(E/Z = 1/10)	45[d]
4	 (E)	B, 49 (45)	 4	(E/Z = 25/1)	35[e]
5	 (E or Z)	B, 20 (16)	 5a : 5b	(1.5 : 1)	51[f]
					
6	R = Ph	B, 21 (14)	6a (44) : 6b (43) : 6' (13)		36[f]
7	R = COOEt	B, 42 (40)	7a (44) : 7b (36) : 7' (11)		58[f]
8	 (E,E)	A, 24 (18)	 (R*,R*)-10	(>95% R*,R*) (>99% E)	55[g]
9	 (E,Z)	A, 24 (0)	 (R*,S*)-10	(>95% R*,S*) (>99% E)	62[g]
10		B, 5 (3)	 11	(>98% cis)	89[g]
11		A, 10 (3)	 12	(>97% cis)	55[g]
12		B, 4.5 (0.5)	 13 (57) : 14 (43)	($\alpha CH_3/\beta CH_3$ = 1/4) (= 4/1)	65[g]
13		B, 12 (0)	 15	(>98% cis)	74[g]
14		B, 72 (0)	 16	(>95% β,β,α)	58[g]
15		B, 36 (0)[h]	 17 : 17'	(3 : 1)	61

[a] The amount of Pd(II) catalyst was 5 mol % for cyclic and 7.5 mol % for acyclic dienes. Method A: a two-phase system (HOAc/pentane) was used. Method B: a one-phase system (HOAc) was used. [b] Contaminated with $CH_2=CH-CH(Cl)CH_2OAc$ (1') (9%). [c] Contaminated with 2' (4%) and $ClCH_2-CH=C(CH_3)CH_2OAc$ (20) (8%). [d] Contaminated with $CH_2=CCH_3-CCH_3(Cl)CH_2OAc$ (3') (9%). [e] Contaminated with $CH_3CH=CH-CCH_3(Cl)CH_2OAc$ (7%). [f] >95% *E* configuration. [g] >99% 1,4-addition. [h] Seven equivalents of $LiOAc\cdot 2H_2O$ and 1.2 equivalents of LiCl were used, and the reaction was performed at 43 °C.

dation reactions are catalyzed by palladium(II) and proceed via a (π-allyl)palladium intermediate (Scheme I). The addition of the nucleophiles X and Y is stereo- and regioselective, and importantly, the stereochemistry of the attack by the second nucleophile Y can be controlled in some cases to proceed either from the opposite side (trans attack) or from the same side (cis attack) as the metal atom. Three principal reactions, 1,4-diacetoxylation,[7a,b] 1,4-acetoxychlorination,[7c] and 1,4-acetoxytrifluoroacetoxylation[7d] have been reported which all have their specific synthetic advantages. In this paper, we give a complete account of the 1,4-acetoxychlorination reaction, discuss the mechanism, and demonstrate its synthetic utility in selective organic transformations.

Scheme I



Results

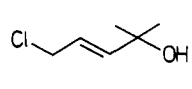
1,4-Acetoxychlorination. Palladium-catalyzed oxidation of conjugated dienes in acetic acid in the presence of LiCl and LiOAc proceeds smoothly, to selectively produce 1-acetoxy-4-chloro-2-alkenes (eq 1, Table I). All reactions were performed at room

(7) (a) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959. (b) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619. (c) Bäckvall, J. E.; Nordberg, R. E.; Nyström, J. E. *Tetrahedron Lett.* **1982**, *23*, 1617. (d) Bäckvall, J. E.; Vågberg, J.; Nordberg, R. E. *Tetrahedron Lett.* **1984**, *25*, 2717.

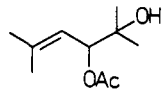
$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{p-benzoquinone}\\ \text{HOAc, 25°C}]{\text{cat. Pd(OAc)}_2\\ \text{LiCl, LiOAc}} -\overset{|}{\underset{Cl}{C}}-C=C-\overset{|}{\underset{OAc}{C}}- \qquad (1)$$

temperature, and the oxidant used was *p*-benzoquinone which was found to have a remarkable ability to promote a stereo- and regioselective acetoxychlorination. A number of dienes were tested and so far only two dienes, 1,3-cyclopentadiene and 1-acetoxy-2,4-hexadiene, failed to give an oxidation product under the present reaction conditions. Interestingly, 4-methyl-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene gave no chloroacetate but afforded the chloro alcohol **8** and hydroxyacetate **9**, respectively.[8]

The chemoselectivity for chloroacetate over diacetate and dichloride is high and usually exceeds 99%. On prolonged reaction time, however, a few percent of diacetate was observed in some



8



9

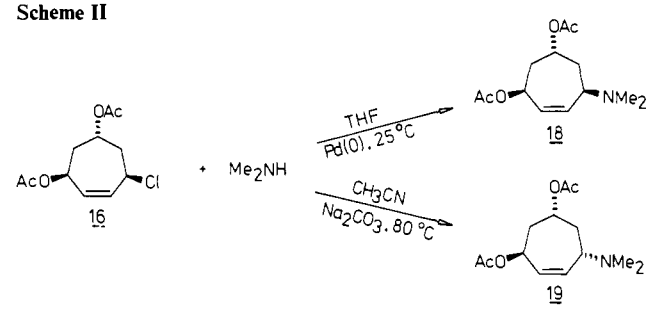
cases due to a secondary substitution reaction, but the ratio chloroacetate/diacetate was always >20. The amount of dichloride was usually under the detectable limit, i.e., chloroacetate/dichloride >100. In the case of butadiene, we determined the ratio 1-acetoxy-4-chloro-2-butene/1,4-dichloro-2-butene to be 260:1.

The amount of palladium catalyst utilized (usually $Pd(OAc)_2$ but Li_2PdCl_4 gives identical results) was 5 mol % for cyclic dienes and 7.5 mol % for acyclic dienes. These amounts were used for convenience in the laboratory procedure, but the reaction works in several cases with a much lower amount of catalyst.[9] For example, the oxidation of 1,3-cyclohexadiene using 0.2 mol % $Pd(OAc)_2$ selectively produced the chloroacetate in an isolated yield of 60% which corresponds to 300 turnovers.

The acetoxychlorination of acyclic dienes can, a priori, give a product with either an *E* or *Z* double bond. When the 1,3-diene is unsubstituted in the 2- and 3-position, the 1,4-chloroacetate formed is almost exclusively of the *E* configuration (90–100%, entries 1, 5–7, 8, and 9). The highest degree of *E* stereochemistry was obtained for the 2,4-hexadienes which furnished products with >99% *E* geometry of the double bond (entries 10 and 11). A substituent in the 2- and/or 3-position increased the amount of *Z* product (entries 2–4). In the series butadiene, isoprene, (*E*)-2-methylpentadiene, and 2,3-dimethylbutadiene, the *E*/*Z* ratio decreased and was 9/1, 3.6/1, 2.5/1, and 1/10, respectively (entries 1, 2, 4, and 3).

The acetoxychlorination is highly stereospecific, and cyclic dienes afforded products with >97–98% cis stereochemistry. The ^1H NMR spectrum of the product **11** from 1,3-cyclohexadiene (entry 10) is consistent with a cis configuration and shows the CH_2–CH_2 grouping more *concentrated* than in the corresponding trans isomer.[7a,b] Conclusive evidence for the cis stereochemistry of **11** follows from its transformation to the known[7a,b] *trans*-1,4-diacetoxy-2-cyclohexene by reaction with KOAc in Me_2SO. Also the selective transformations of **11** performed previously[7c] confirms the cis configuration of **11**. Interestingly, the stereospecific addition could be extended to acyclic systems. Palladium-catalyzed acetoxychlorination of (*E*,*E*)-2,4-hexadiene selectively produced a single diastereoisomer (*R**,*R**)-**10** (entry 8) which corresponds to an overall cis addition of Cl and OAc across the S-trans conformation of the diene. In an analogous manner (*E*,*Z*)-2,4-hexadiene selectively afforded (*R**,*S**)-**10** (entry 9). The diastereomeric purity (>95%) of (*R**,*R**)- and (*R**,*S**)-**10** was determined by ^1H NMR. The configurational assignments of (*R**,*R**)- and (*R**,*S**)-**10** were made in analogy with the products from the corresponding palladium-catalyzed diacetoxylation,[7b] and it was confirmed by chemical transformations (vide infra).

Scheme II



The 1,4-regioselectivity is usually high. For the 2,4-hexadienes and the cyclic dienes, except 1,3-cyclooctadiene, the regioselectivity for 1,4-addition is complete and no 1,2-adduct could be detected in the crude product (>99% 1,4-addition). 1,3-Cyclooctadiene was the only case of those studied where the use of *p*-benzoquinone as the oxidant gave a considerable amount of 1,2-isomer. This diene afforded 1,4-chloroacetate **17** and 1,2-chloroacetate **17′** in a ratio of 3:1, with a cis configuration of both isomers (entry 15). The relative amount of 1,2-adduct among the acyclic dienes having at least one terminal double bond varied between 4% and 13% (entries 1, 2, and 3–7). When *p*-benzoquinone was replaced by MnO_2 as the oxidant, the relative amount of 1,2-addition increased to 25–40%.

The regioselectivity in the oxidation of an unsymmetrically substituted diene was investigated for both cyclic and acyclic dienes. A methyl group in the 2-position directed the chloro group to the 1-position, and a 4-acetoxy-1-chloro–2-methyl-2-alkene was selectively formed (entries 2, 4, and 11). This regioselectivity is of great use in the synthetic transformations of the chloroacetates (vide infra). On the other hand, the regioselectivity obtained with substituents in the 1-position was less general. Thus, 1,3-pentadiene and related 1,3-dienes showed a slight preference for the chloroacetate in which acetate has attacked the most substituted carbon (entry 5–7). 4-Methyl-1,3-pentadiene, on the other hand, gave a highly regioselective reaction, but in this case, the product was the 1,4-chloro alcohol **8**.

To determine the diastereoselectivity of the reaction toward a chirality in the diene, cyclic dienes with a substituent outside the diene unit were studied. In particular the directing effect of an allylic or homoallylic substituent is of interest. Acetoxychlorination of 6-acetoxy-1,3-cycloheptadiene (entry 14) afforded only one isomer according to ^1H NMR, GLC, and HPLC. In analogy with the palladium-catalyzed diacetoxylation of the same diene,[7b] we have assigned it as the 1β, 4β, 6α-isomer **16**. The ^1H NMR spectrum of **16** is consistent with this configuration. The selective functionalization reactions shown in Scheme II, where the chloro group is substituted with either retention or inversion, confirms the stereochemistry of **16**.

Palladium-catalyzed 1,4-acetoxychlorination of 5-methyl-1,3-cyclohexadiene was less selective (entry 12). Two regioisomers were formed in a ratio of 57:43, and each regioisomer was found to be a 4:1 mixture of diastereoisomers due to the 5-methyl group.

One disturbing side reaction in the 1,4-acetoxychlorination reaction is Diels–Alder addition between the diene and *p*-benzoquinone. This reaction could be depressed by keeping the diene concentration low in the reaction mixture. This was achieved by slow addition of the diene and/or by the use of a two-phase system (acetic acid–pentane).[7b] For the cyclic dienes (entries 10–15), the relative yield of Diels–Alder product thus was usually <5% in the crude product. For the acyclic dienes, the relative yield of Diels–Alder product varied from 5% to 20%. The Diels–Alder side product was readily removed from the product by several methods (see Experimental Section).

Because of the above mentioned side reaction, we tried to replace *p*-benzoquinone by other oxidants. Attempts to use chloranil or methyl-substituted benzoquinones failed and gave no reaction or a very slow reaction. When *p*-benzoquinone was replaced by MnO_2 or urea hydroperoxide, a much lower regio-

(8) Due to the use of $LiOAc{\cdot}2H_2O$, the acetic acid phase contains ≈2% of water (by weight) which apparently has attacked in place of acetate: Nyström, J. E., unpublished results.

(9) Byström, S. E.; Bäckvall, J. E.; Nordberg, R. E.; Nyström, J. E. Swedish Patent 8201 911-8, 1982.

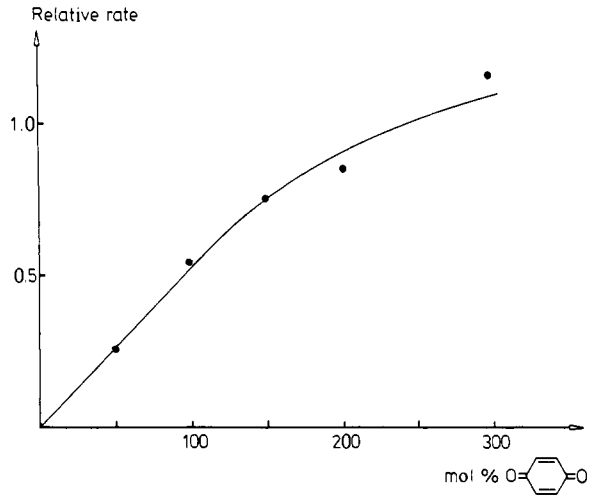


Figure 1. Relative initial rate for the palladium-catalyzed 1,4-acetoxychlorination of 1,3-cyclohexadiene as a function of the amount of *p*-benzoquinone using 5 mol % $Pd(OAc)_2$.

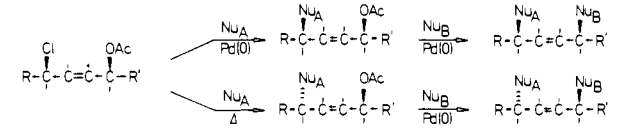
Table II. (a) Competitive Experiments and (b) Absolute Relative Rates

a		b	
diene	rate	diene	rate
(*E*,*Z*)-2,4-hexadiene	1	(*Z*)-1,3-pentadiene	1
(*E*,*E*)-2,4-hexadiene	1.9	(*E*)-1,3-pentadiene	2.3
isoprene	3.8	(*E*,*Z*)-2,4-hexadiene	4.4
1,3-cyclohexadiene	50	(*E*,*E*)-2,4-hexadiene	8.3

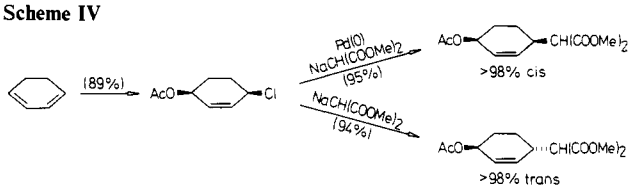
and stereospecificity was obtained. For example, palladium-catalyzed acetoxychlorination of isoprene using MnO_2 as the oxidant (at 40 °C) produced the 1,4-isomer (*E*)-**2** and the 1,2-isomer 4-acetoxy-3-chloro-2-methyl-1-butene (**2'**) in a ratio of 1.5:1. Interestingly, the 1,4-isomer was exclusively of *E* configuration (>95% *E*). This is in contrast to the 1,4-isomer obtained by using *p*-benzoquinone as the oxidant, which gave an *E*/*Z* ratio of 3.6/1 (entries 2a and 2b). Also, 1,3-cyclohexadiene, when oxidized with MnO_2 (at 40 °C), afforded a considerable amount of 1,2-isomer (1,2:1,4 = 15:85), and furthermore the 1,4-isomer was a cis and trans mixture (cis/trans = 1:3).[10] We also tried $CuCl_2$ as the oxidant, since it is known that olefins are oxidized to vicinal chloroacetates in acetic acid by a $Pd(II)/CuCl_2$ system, however, with low product selectivity.[11,12] Palladium-catalyzed oxidation of butadiene in acetic acid using $CuCl_2/O_2$ as the oxidant (pO_2 = 5 kg/cm^2) proceeded very slowly and gave only two turnovers after 22 h. The 1,4/1,2 ratio was approximately 4/1. Finally, the use of isoamyl nitrite in the oxidation of butadiene afforded 1,4-dichloro-2-butene as the only oxidation product.

The use of *p*-benzoquinone therefore seems to be essential for an efficient and selective reaction. We previously found[7b] that in the related palladium-catalyzed 1,4-diacetoxylation, the dependence of the benzoquinone concentration on the reaction rate could be interpreted as benzoquinone acting also as a ligand. The dependence of the *p*-benzoquinone concentration on the rate of the palladium-catalyzed 1,4-acetoxychlorination of 1,3-cyclohexadiene is shown in Figure 1. The figure reveals that the rate of the oxidation increases linearly with the concentration of *p*-benzoquinone up to 120 mol % and then the increase becomes smaller.

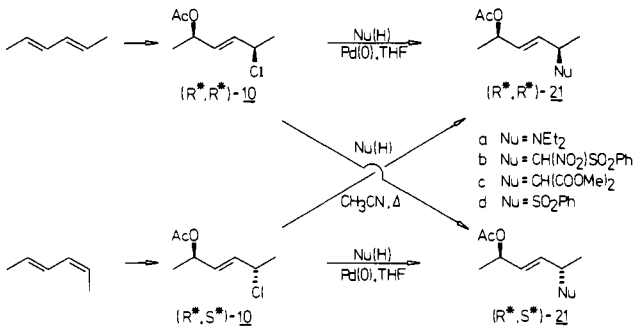
Scheme III



Scheme IV



Scheme V



The relative rates of the oxidation of some dienes were investigated and are given in Table II. The relative rates were determined either via competitive experiments (Table IIa) or via direct measurements of the rate in individual experiments (Table IIb). The competitive experiments may give wrong relative rates if a competition occurs in the coordination step and if one diene coordinates strongly and completely blocks the coordination of the other diene. The relative rates obtained from the absolute rate determinations, however, indicate that this is not the case. Thus, both methods give a ratio of relative rates between (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene of 1.9:1. This increase of the rate by approximately a factor of 2 on changing one double bond from *Z* to *E* was also observed for 1,3-pentadiene (Table IIb). The competitive experiments show that 1,3-cyclohexadiene reacts considerably faster than the acyclic dienes (Table IIa).

Synthetic Applications. An important aspect of the palladium-catalyzed acetoxychlorination reaction described in this paper is that the chloro and acetoxy groups can be sequentially substituted by two different nucleophiles (Scheme III). After a completely chemoselective nucleophilic substitution of the chloro group,[7c,13] the acetoxy group can be substituted in a transition-metal-catalyzed (Pd, Cu, Ni, Mo, and Fe) reaction.[7c,14,15] This allows a *regiochemical choice*, and the principle was applied to the synthesis of the Monarch butterfly pheromone by using the chloroacetate **2** from isoprene.[13] The chloroacetate **2** in this way becomes a useful building block for terpenoid synthesis. More generally the chloroacetate products can be considered as useful multiple coupling reagents (MCR),[16] with two electrophilic sites.

Importantly, the substitution reactions in Scheme III are stereospecific, which allows the creation of new carbon–carbon bonds

(10) It is remarkable that MnO_2 works as an oxidant in the palladium-catalyzed acetoxychlorination, since it is extremely slow in the corresponding palladium-catalyzed diacetoxylation. We believe that this may be explained by an increase in oxidation potential of Mn(IV) in acetoxychlorination due to the presence of chloride ions.

(11) (a) Henry, P. M. "Palladium-Catalyzed Oxidation of Hydrocarbons"; D. Reidel: Dordrecht, 1980. (b) Henry, P. M. *J. Org. Chem.* **1974**, *39*, 3871; *J. Am. Chem. Soc.* **1972**, *94*, 7305. (c) Bäckvall, J. E. *Tetrahedron Lett.* **1977**, 467.

(12) For oxidation of nonconjugated dienes using the Pd^{II}–$CuCl_2$ system in acetic acid, see: Heuman, A.; Waegell, B. *Nouv. J. Chem.* **1977**, *1*, 275. Heumann, A. Reglier, M., Waegell, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 866, 867; *Tetrahedron Lett.* **1983**, *24*, 1971.

(13) Nyström, J. E.; Bäckvall, J. E. *J. Org. Chem.* **1983**, *48*, 3947.

(14) (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. (d) Trost, B. M.; Verhoeven, T. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, p 799.

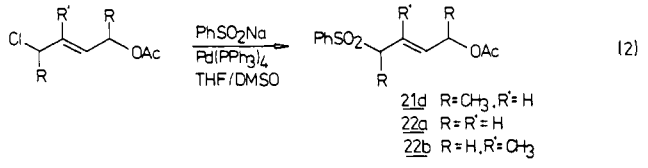
(15) (a) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901. (b) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318. (c) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Ibid.* **1981**, *103*, 6863. (d) Trost, B. M.; Lautens, M. *Ibid.* **1981**, *103*, 5543. Roustan, J. L.; Marour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, 3721. (f) Goering, H. L.; Seitz, E. P.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304.

(16) Seebach, D.; Knochel, P. *Helv. Chim. Acta* **1984**, *67*, 261.

with control of the 1,4-relative stereochemistry. Other methods for obtaining a similar control of the 1,4-relative stereochemistry at carbon include transition-metal-catalyzed nucleophilic additions to 1,3-diene monoepoxides.[17,18] An advantage of the acetoxychlorination approach over the metal-catalyzed nucleophilic addition to 1,3-diene monoepoxide is that it offers a *stereochemical choice* (Scheme III). By applying either a metal-catalyzed reaction or a classical S_N2 reaction, the chloro group can be displaced with either retention or inversion at carbon. This was previously demonstrated on the chloroacetate **11** from 1,3-cyclohexadiene,[7c] and the principle was also shown on the chloroacetate **16** from 6-acetoxy-1,3-cycloheptadiene (Scheme II). In this way, a great number of 1,4-disubstituted 2-cycloalkenes with either cis or trans stereochemistry are available by choice. One example (Scheme IV), which illustrates the unique ability of the methodology, is the formal cis or trans 1,4-addition of the groups AcO– and $(MeOOC)_2CH$– to 1,3-cyclohexadiene via **11** in an overall yield of 84–85% and with a diastereoselectivity >98%!

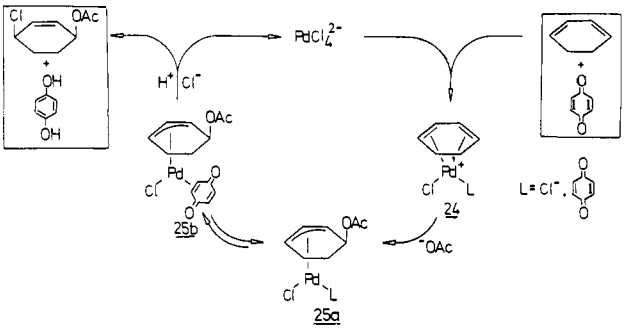
We now also demonstrate how one may obtain a similar stereocontrol in an acyclic system (Scheme V). Reaction of (*R*,R**)-**10** with diethylamine in the presence of $Pd(PPh_3)_4$ afforded (*R*,R**)-**21a** (>92% *R*,R**) in 70% yield. When (*R*,R**)-**10** was allowed to react with diethylamine in acetonitrile in the absence of catalyst, (*R*,S**)-**21a** (>90% *R*,S**) was formed in 82% yield. Analogously, (*R*,S**)- and (*R*,R**)-**21a** were prepared by carrying out the same reactions on (*R*,S**)-**10**. The two possible diastereoisomers (*R*,S**)-**21** and (*R*,R**)-**21** were prepared for three other nucleophiles (**21b**, **c**, and **d**) in a diastereomeric purity of 94–96%. Since the allylic acetoxy group can be stereospecifically replaced by carbon or nitrogen nucleophiles using either palladium[14] or copper[15b,f] catalysis, a great number of acyclic derivatives with a defined 1,4-relative stereochemistry between carbons are available by this method. Such a control of the relative stereochemistry between distant carbons in acyclic systems is a difficult and challenging problem in organic synthesis.[19] General approaches to the construction of remote asymmetric relationships in acyclic systems are rare,[19d,e] and none of the previous methods allow the choice of preparing both diastereoisomers. We recently applied the methodology illustrated in Scheme V to the stereocontrolled synthesis of the (*R*,R**)- and (*R*,S**)-5-hydroxy-2-methylhexanoic acid lactones (pheromone of the carpenter bee) from (*E,E*)- and (*E,Z*)-2,4-hexadiene via the synthetic intermediates (*R*,R**)-**21b** and (*R*,S**)-**21b**, respectively.[20] The group $CH(NO_2)(SO_2Ph)$ served as a carboxy anion equivalent in this synthesis.[21]

We were pleased to find that the phenyl sulfinate anion (as $NaSO_2Ph$) readily displaces the allylic chloro group of the chloroacetates under mild conditions in good yield (71–98%) by using a palladium-catalyzed reaction (eq 2) (cf. (*R*,S**)- and (*R*,R**)-**21d**).[22] The chloroacetate **2** from isoprene was trans-

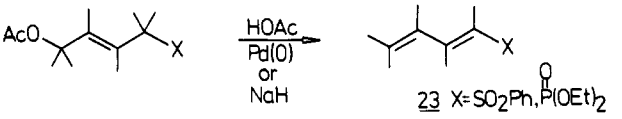


(2)

Scheme VI



formed to the sulfone **22b**. The sulfone **22b** is another versatile isoprene synthon[23,24] with one electrophilic and one nucleophilic center and the hydrolized alcohol of **22b** has been used in a terpenoid synthesis.[23] The 1-acetoxy-4-(phenylsulfonyl)-2-alkenes and the corresponding 1-acetoxy-4-phosphoryl-2-alkenes, readily available from the corresponding chloroacetates via an Arbuzov reaction, were used for the preparation of the synthetically important 1,3-dienes **23**.[25]



By amination of the chloro group either in a palladium-catalyzed substitution or a classical nucleophilic substitution, a great number of 4-amino-alk-2-enyl acetates were prepared.[26,27] Some of these aminoacetates have been cyclized to pyrrole derivatives.[26,27]

Discussion

A likely mechanism for the catalytic cycle of the palladium-catalyzed 1,4-acetoxychlorination is shown for 1,3-cyclohexadiene in Scheme VI). The major inorganic palladium species in solution is most likely monomeric $PdCl_4^{2-}$.[28,29] Coordination of the diene followed by a trans acetoxypalladation[30] of one of the double bonds gives a (π-allyl)palladium intermediate **25**. Although monodentate complexes of conjugated dienes with palladium can form at low temperature,[31] our results are best explained by formation of a cisoid (*S*)-η^4-diene complex **24** before the acetoxypalladation takes place (vide infra).[32] The regioselectivity for acetate attack at C-1 (terminal) could be a result of a thermodynamic control, since it has been shown that nucleophiles initially attack (η^4-1,3-di-

(17) (a) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575. (b) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. (c) Takahashi, T.; Kataoka, H.; Tsuji, J. *J. Am. Chem. Soc.* **1983**, *105*, 147.

(18) (a) Marino, J. P.; Floyd, D. M. *Tetrahedron Lett.* **1979**, 675. (b) Marino, J. P.; Hatonaka, H. *J. Org. Chem.* **1979**, *44*, 4467. (c) Marino, J. P.; Abe, H. *J. Am. Chem. Soc.* **1981**, *103*, 2907. (d) Marino, J. P.; Jaen, J C. *Tetrahedron Lett.* **1983**, *24*, 441. (e) Anderson, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 4978.

(19) (a) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. (b) *Tetrahedron* **1984**, *40*, 2197–2343 (Symp. No. 16, T. Mukayama, Ed.). (c) *Tetrahedron* **1984**, *40*, 1213–1417 (Symp. No. 15, A. I. Meyers, Ed.). (d) Still, W. C.; Darst, K. P., *J. Am. Chem. Soc.* **1980**, *102*, 7387. (e) Fukuyama, T.; Vranesic, B.; Negri, D. P.; Kishi, Y. *Tetrahedron Lett.* **1978**, 2741.

(20) Bäckvall, J. E.; Byström, S. E.; Nyström, J. E. *Tetrahedron*, in press.

(21) Wade, P. A.; Hinney, H. R.; Amin, N. W.; Vail, P. D.; Morrow, S. D.; Hardinger, S. A.; Saft, M. S. *J. Org. Chem.* **1981**, *46*, 765.

(22) Attempts to substitute the chloro group in the chloroacetates with the phenyl sulfinate anion in an ordinary S_N2 reaction was less convenient and required higher temperature. Substitution of **2** ($NaSO_2Ph$, DMF, 60 °C) has been reported.[23]

(23) Olson, G. L.; Cheung, H. C.; Morgan, K. D.; Neukom, C.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3287.

(24) (a) Cainelli, G.; Cardillo, G. *Acc. Chem. Res.* **1981**, *14*, 89. (b) Julia, M.; Verpeux, J. N. *Tetrahedron* **1983**, *39*, 3289

(25) Åkermark, B.; Nyström, J. E.; Rein, T.; Bäckvall, J. E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719.

(26) Genêt, J. P.; Balabane, M.; Bäckvall, J. E.; Nyström, J. E. *Tetrahedron Lett.* **1983**, *24*, 2745.

(27) Nyström, J. E.; Bäckvall, J. E., unpublished results.

(28) (a) Goldberg, R. N.; Hepler, L. G. *Chem. Rev.* **1968**, *68*, 229. (b) Aguilo, A. *Adv. Organometal. Chem.* **1967**, *5*, 327.

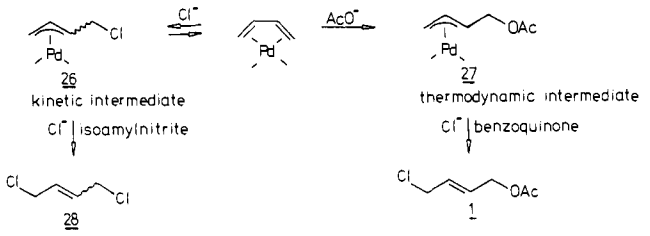
(29) (a) Although an ultraviolet study of $PdCl_2$–LiCl solutions in anhydrous acetic acid (<0.02% water) indicated the presence of dimeric $Li_2Pd_2Cl_6$[29b] at low chloride concentration, our major species is most likely the monomeric complex for two reasons: (i) the concentration of LiCl is usually 40 times higher then the Pd(II) concentration; (ii) we are working in acetic acid containing 2% water (it is known that Pd(II) exists exclusively as $PdCl_4^{2-}$ in water above a chloride concentration of 0.1 M[28]). (b) Henry, P. M.; Marks, O. W. *Inorg. Chem.* **1971**, *10*, 373.

(30) (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.

(31) Donati, F.; Conti, F. *Tetrahedron Lett.* **1966**, 1219.

(32) Treatment of (4-chloro-1,2,3-η^3-alkenyl)palladium chloride with superacids has in fact been shown to form η^4 complexes related to **24** (L = SbF_5Cl): Lukas, J.; Kramer, P. A. *J. Organomet. Chem.* **1971**, *31*, 111.

Scheme VII



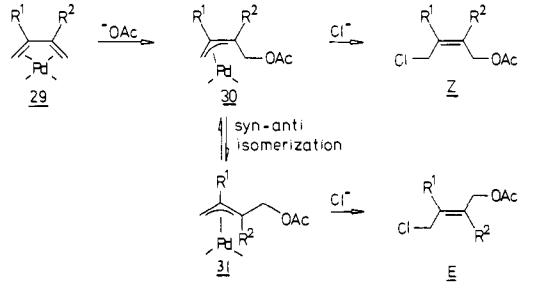
ene)iron complexes at C-2 (internal), followed by rearrangement to the C-1 adduct.[33] Coordination of *p*-benzoquinone followed by an external trans attack by a chloride ion accounts for the overall cis stereochemistry observed. The high stereospecificity shows that no cis migration of chloride from palladium to carbon takes place. Thus, it seems that migration of coordinated chloride from palladium to a coordinated carbon (cf. reductive elimination) is an unfavored process as suggested previously.[34]

It is likely that *p*-benzoquinone coordinates to palladium and in this way facilitates the electron-transfer process. Moiseev and co-workers[35] reported that treatment of (π-allyl)palladium chloride with *p*-benzoquinone and aqueous HCl gave allyl chloride, and the kinetics of the reaction were consistent with a coordination of the benzoquinone. Stable *p*-benzoquinone complexes of nickel(0), palladium(0), and platinum(0) have been described,[36] and protonation of a (*p*-benzoquinone)nickel(0) complex was shown to yield hydroquinone and nickel(II).[36c]

The first-order dependence of *p*-benzoquinone on the reaction rate (Figure 1) supports a coordination of the quinone. Because of the strongly coordinated chloride ligands, a large excess of *p*-benzoquinone (30-fold to palladium) is required before the linear increase of the rate is declining.[7b]

The high product selectivity for chloroacetate over diacetate and dichloride is remarkable. From a statistical point of view, one would expect the latter products to form to some extent. The regiochemistry observed for isoprene (Table I, entry 2) supports that the first nucleophile introduced is acetate, since isoprene is known[37] to react with palladium chloride in acetic acid to give (4-acetoxy-2-methyl-1,2,3,-η^3-butenyl)palladium chloride dimer. The question is, why does acetate win in the first step when chloride wins in the second step. An explanation for this unusual selectivity is offered in Scheme VII. The chloro complex **26**, if initially formed, is expected to solvolyze rapidly in acetic acid (via diene complex) to afford the more stable complex **27**.[33,38] External chloride attack on **27** would give the observed chloroacetate **1** as the sole product. Further support for a chloro complex **26** as a kinetic intermediate is provided by the formation of 1,4-dichloro-2-butene (**28**) when *p*-benzoquinone was replaced by the more rapid oxidant isoamyl nitrite.[27,39] It is interesting to note that a chlorometalation adduct was detected as the initial intermediate in oxymetalation of ethene when using platinum chloride.[40]

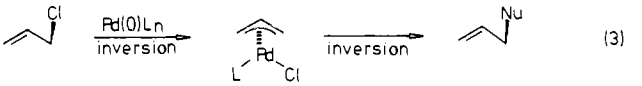
Scheme VIII



The variation of the E/Z ratio of the acyclic chloroacetates with the substrates and reaction conditions can be explained if one assumes that a (*S*)-η^4-coordinated cisoid diene complex **29** is formed initially (Scheme VIII). Acetate addition to the complex **29** would give mainly complex **30**. A syn–anti isomerization would produce complex **31**, which is considerably more stable than **30** if R^2 = H. When R^1 = R^2 = H, the isomerization of **30** to **31** should be rapid and the *E* product is expected as the major isomer, which is observed for butadiene (E/Z = 9/1). On the other hand, for 2,3-dimethylbutadiene, the isomerization of complex **30** (R^1 = R^2 = CH_3) to **31** is small. This explains the predominant formation of *Z* product from this diene (E/Z = 1/10). For isoprene the rate of isomerization of **30** (R^1 = CH_3, R^2 = H) to **31** falls in between, which would explain the observed E/Z ratio of = 3.6/1. Also, the observed increase of the acetoxychlorination rate by a factor of 2 on changing one double bond from *Z* to *E* is consistent with a cisoid η^4-coordinated diene (cf. Table IIa and b). Such a coordination would be more difficult for a (*Z*)-diene than for an (*E*)-diene.

The regioselectivity obtained for unsymmetrically substituted dienes is nicely explained by considering the π-allyl intermediates. Thus, a substituent in the 2-position of the 1,3-diene will lead almost exclusively to the more stable (π-allyl)palladium complex.[37] Furthermore, the low regioselectivity obtained for 1-substituted 1,3-dienes is consistent with the observation that reaction of 1,3-pentadiene with Pd(II) in methanol produces two isomeric π-allyl complexes.[37a]

The highly stereospecific palladium(0)-catalyzed substitution reactions of the allylic chloride that take place with complete retention proceed via the mechanism outlined in eq 3 in analogy with the palladium(0)-catalyzed nucleophilic substitution reactions of allylic acetate. The reason for the high stereospecificity



(3)

compared to the reaction of allylic acetate is that the coordinated chloro group has no tendecy to migrate to the allyl group (vide supra), which is the case for a coordinated acetoxy group.[7a,b,41,42] Such a cis migration will lead to isomerization of the starting allylic substrate.[41,43]

It is interesting to note that the acyclic (π-allyl)palladium complexes **32**, which occur as intermediates in the oxidation of 2,4-hexadienes as well as in the palladium(0)-catalyzed substitutions, are configurationally stable. Diastereomeric complexes related to **32** have been shown to be configurationally stable,[44] and recently, the optically active (π-allyl)palladium complex **33** was prepared and shown not to racemize.[45,46]

(33) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715.

(34) (a) Bäckvall, J. E.; Björkman, E. E. *J. Chem. Soc., Chem. Commun.* **1982**, 693. (b) Bäckvall, J. E.; Björkman, E. E.; Petterson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369.

(35) Satsko, N. G.; Below, A. P.; Moiseev, I. I. *Kinet. Catal.* **1972**, *13*, 892; *Chem. Abstr.* **1973**, *78*, 83584c.

(36) (a) Hiramatsu, M.; Nakano, H.; Fujinami, T.; Sakai, S. *J. Organomet. Chem.* **1982**, *236*, 131. Hiramatsu, M.; Shiozaki, K.; Fujinami, T.; Sakai, S. *Ibid.* **1983**, *246*, 303. (b) Chetcuti, M. J.; Howard, J. A. K.; Pfeffer, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 276. Chetcuti, M. J.; Herbert, J. A.; Howard, J. A. K. Pfeffer, M.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *Ibid.* **1981**, 284. (c) Uhlig, E.; Fischer, R.; Kirmse, R. *J. Organomet. Chem.* **1982**, *239*, 385.

(37) (a) Rowe, J. M.; White, D. A. *J. Chem. Soc. A* **1967**, 1451. (b) Levanda, O. G.; Pek, G. I.; Moiseev, I. I. *Zh. Org. Khim.* **1971**, *7*, 217.

(38) Such exchange reactions of the chloro group in (4-chloro-1,2,3-η^3-alkenyl)palladium complexes related to **26** are well-known: (a) Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1963**, 4806. (b) Åkermark, B.; Bäckvall, J. E.; Löwenborg, A.; Zetterberg, K. *J. Organomet. Chem.* **1979**, *166*, C33.

(39) The dichloride **28** was a mixture of the *E* and *Z* isomer in a ratio of 1:1.4, which reflects a competition between syn–anti isomerization and nucleophilic attack similar to that shown in Scheme VIII.

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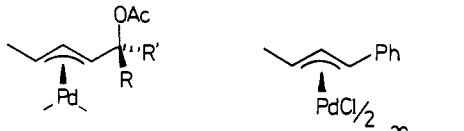

32 R = H, R' = CH_3
R = CH_3, R' = H

33 $(\alpha)_D^{20} = -579°$

It should be mentioned that the sequential nucleophilic substitution of the chloroacetates outlined in Scheme III can be performed in one pot. This was used for a highly selective sequential dialkylation of chloroacetate **2** by using two different carbon nucleophiles.[13] Related sequential palladium-catalyzed nucleophilic substitutions were recently performed on (*Z*)-4-acetoxybut-2-enyl diethyl phosphate[47] and 2-cyclopentene-1,4-diol dicarboxylates.[48] A discrete two step alkylation has also been used to prepare vinylcyclopropanes from 2-alkene-1,4-diol derivatives.[49]

Concluding Remark

The present work has shown that conjugated dienes can be selectively oxidized to the synthetically useful 1-acetoxy-4-chloro-2-alkenes under mild conditions (room temperature) by using a Pd(II) salt as the catalyst (0.2–7.5 mol %). The mechanism of the acetoxychlorination is now well understood. It proceeds via a (4-acetoxy-1,2,3-η^3-allyl)palladium intermediate, followed by an oxidation-induced attack by chloride.

The reaction is 1,4-regioselective in most cases. Furthermore, the acetoxychlorination is highly stereospecific in both cyclic and acyclic systems. This constitutes a useful internal 1,4-asymmetric induction. Combined with the fact that the chloro group can be substituted with *either* retention or inversion, the acetoxychlorination approach allows a complete control of the 1,4-relative stereochemistry. Such a dual control of the 1,4-relative stereochemistry with the unique choice of 1,4-functionality is previously unprecedented in organic chemistry.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. NMR spectra were obtained with a Bruker WP 200 FT spectrometer, ^1H NMR at 200 MHz, and ^{13}C NMR at 50.3 MHz. ^{13}C NMR multiplicities were obtained by proton off-resonance decoupling at 1650 Hz. Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane, Me_4Si. High-pressure liquid chromatography (HPLC) was performed on a Waters M-45 instrument with a micro-Porasil column (silica, 10-μm packing, 0.4 × 30 cm) and a differential refractometer as detector. The slow diene additions were performed with a Sage Instruments Model 355 syringe pump. Bulb-to-bulb distillations were performed with a Büchi Kugelrhor apparatus.

Butadiene, isoprene, 2,3-dimethylbutadiene, (*E*)-2-methyl-1,3-pentadiene, (*E*)- and (*Z*)-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene were purchased from FLUKA AG and were distilled before use. (*E*)-6-Phenyl-1,3-hexadiene,[50] ethyl (*E*)-4,6-heptadienoate,[51] and 2-methyl- and 5-methyl-1,3-cyclohexadiene[7b,52] were prepared according to literature procedures. 6-Acetoxy-1,3-cycloheptadiene was prepared by acetylation (Ac_2O, 4-(dimethylamino)pyridine, and Et_3N) of 6-hydroxy-1,3-cycloheptadiene.[7b,53] Palladium acetate was purchased from Engelhard Industries. Lithium acetate dihydrate, lithium chloride, *p*-benzoquinone, and sodium benzenesulfinate were 99% grade and were used without further purification. Tetrahydrofuran (THF) was distilled from a deep blue solution of potassium/benzophenone. Acetonitrile was distilled over CaH_2 and stored over molecular sieves (4 Å).

Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$). To a homogeneous, brown, stirred solution of $Pd(PhCN)_2Cl_2$ (3.07 g, 8.0 mmol) in degassed acetone (80 mL) under nitrogen at 0 °C was added butadiene (1.8 g, 33 mmol), which resulted in formation of a yellow precipitate. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 2 h. The mixture was cooled to 0 °C, and diethylamine (6.7 mL, 64 mmol) was added. Triphenylphosphine (8.4 g, 32 mmol) was immediately added and a precipitation of the yellow Pd(0) complex was observed. After the mixture was stirred at 0 °C for 1 h, the crystals were filtered off under nitrogen by using a glass filter (Schlenk apparatus). The crystals were washed under nitrogen with ice-cold degassed solvents: acetone (2 × 20 mL), acetone/water 1/1 mixture (2 × 20 mL), and finally acetone (2 × 20 mL). The complex was dried in vacuo to give 6.41 g (69%) of a light yellow powder. The palladium complex can be stored under nitrogen in a freezer for months.

General Procedures for Palladium(II)-Catalyzed 1,4-Acetoxychlorination of Conjugated Dienes. Unless otherwise noted, all reactions were performed at 25 °C in acetic acid using $Pd(OAc)_2$ as catalyst (5 mol % for the cyclic dienes and 7.5 mol % for the acyclic dienes). The amount of diene used was 0.25–0.30 mmol/mL of acetic acid. Two equivalents of *p*-benzoquinone, LiCl, and $LiOAc{\cdot}2H_2O$ were used.

Method A. The diene was added to the pentane phase of a biphasic pentane/acetic acid reaction mixture (1.5–2.0/1, pentane/HOAc, v/v).

Method B. The diene was added to a monophasic acetic acid reaction mixture. The total reaction time and the diene addition time are shown in Table I. The longer addition times (>3 h) of the diene were accomplished by using a syringe pump.

The results are shown in Table I. The yields refer to isolated yield of distilled product unless otherwise stated. Complete, representative experimental procedures are described for the preparation of **1** (method A and B), **11** (method B), and **12** (method A). For a purification procedure, see under **1**, **6**, or **7**.

(*E*)-1-Acetoxy-4-chloro-2-butene (1) was prepared by either method A (81%) or method B (78%).

Method A. To butadiene (5.40 g, 100 mmol) dissolved in pentane (800 mL) at 0 °C was added an acetic acid (400 mL) solution of $Pd(OAc)_2$ (1.68 g, 7.5 mmol), LiCl (8.4 g, 200 mmol), $LiOAc{\cdot}2H_2O$ (20.4 g, 200 mmol), and *p*-benzoquinone (21.6 g, 200 mmol). After the solution was stirred for 26 h at 25 °C, brine (300 mL) and ether (160 mL) were added, and stirring was continued for another 5 min. The organic phase was separated and the aqueous phase filtered and extracted with pentane/ether (3 × 300 mL, 80/20). The combined organic phases were washed with water (100 + 50 mL), saturated aqueous K_2CO_3 (3 × 100 mL), and 2 M NaOH (3 × 100 mL). The alkaline aqueous phases were back-extracted with pentane/ether (2 × 100 mL, 80/20). The combined organic phases were washed with brine and dried ($MgSO_4$). The solvent was distilled off at ambient pressure and finally rotary-evaporated at reduced pressure, giving a crude product (≈15 g) which was then distilled (10 mmHg, 70–90 °C), yielding 12.0 g (81%) of **1** as a light yellow liquid consisting of (*E*)-**1** (82%), (*Z*)-**1** (9%), and 4-acetoxy-3-chloro-1-butene (**1′**) (9%) according to ^1H NMR. The chloroacetate was contaminated with ≈1% of 5,8-dihydronaphthoquinone: IR (neat) 2940, 1740, 1380, 1360, 1230, 1025, 970 cm^{-1}. Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.11. Found: C, 48.68; H, 5.99.

(*E*)-**1**: ^1H NMR ($CDCl_3$) δ 5.9 (br s, 2 H, CH=CH), 4.59 (br s, 2 H, CH_2OAc), 4.08 (br s, 2 H, CH_2Cl), 2.09 (s, 3 H, AcO); ^{13}C NMR ($CDCl_3$) δ 170.4 (s, CH_3COO), 129.7 (d, one of HC=CH), 128.5 (d, one of HC=CH), 63.56 (t, CH_2OAc), 43.82 (t, CH_2Cl), 20.79 (q, CH_3COO).

(*Z*)-**1** (distinguishable peaks in mixture with (E)-**1** and **1′**): ^1H NMR ($CDCl_3$) δ 4.68 (br d, J = 6 Hz, 2 H, CH_2OAc), 4.15 (br d, J = 6 Hz, 2 H, CH_2Cl).

1′ (distinguishable peaks in mixture with (*E*)- and (*Z*)-**1**): ^1H NMR ($CDCl_3$) δ 5.4 (d, J = 17 Hz, 1 H, trans in CH_2=CH), 5.28 (d, J = 10 Hz, 1 H, cis in CH_2=CH), 4.45–4.20 (AB part of ABX, 2 H, CH—CH_2OAc).

5,8-Dihydronaphthoquinone (distinguishable peaks in mixture with **1**): ^1H NMR ($CDCl_3$) δ 6.7 (s, 2 H, C—CH=CH—C=O), 3.08 (s, 4 H, CH_2).

Purification of 1. **1** (9 g containing ≈ 0.2 g of 5,8-dihydronaphthoquinone) dissolved in ether (150 mL) was stirred with an aqueous 2 M NaOH solution saturated with $NaBH_4$ (10 mL) until the yellow color had disappeared (15 min). The aqueous phase (brown) was discarded and the etheral phase was washed with 2 M NaOH (5 mL) and dried ($MgSO_4$). Concentration at ambient pressure and finally rotary evaporation afforded 8.5 g of **1** as a colorless liquid which was free from 5,8-dihydronaphthoquinone (<0.1%) according to ^1H NMR.

Method B. To a well-stirred solution of $Pd(OAc)_2$ (90 mg, 0.4 mmol), LiCl (336 mg, 8 mmol), $LiOAc{\cdot}2H_2O$ (816 mg, 8 mmol), and *p*-benzoquinone (950 mg, 8.8 mmol) in acetic acid (14 mL) at 25 °C was slowly

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added butadiene dissolved in acetic acid (1.94 g × 1.88 *m* = 3.64 mmol) with a syringe (using a syringe pump) over 16 h. After additional stirring for 4 h, the reaction mixture was diluted with water (8 mL) and pentane/ether (20 mL, 80/20). The workup was the same as in method A. Bulb-to-bulb distillation afforded 422 mg (78%) of **1** with the same composition as that obtained from method A.

1-Acetoxy-4-chloro-3-methyl-2-butene (2) was prepared from isoprene by method A (76%), 22 (0) h, or method B (74%), 26 (16) h.[13] The product consisted of (E)-**2** (69%), (*Z*)-**2** (19%), 4-acetoxy-3-chloro-2-methyl-1-butene (**2′**) (4%), and 1-acetoxy-4-chloro-2-methyl-2-butene (**20**) (8%).

Mixture of (*E*)-2 and 2′ was prepared from isoprene by method A (65%), 14 (0) h, but benzoquinone was replaced by MnO_2. The product consisted of **2** (>95% *E*) (53%), **2′** (34%), **20** (7%), and 4-acetoxy-3-chloro-3-methyl-1-butene (**20′**) (6%) according to ^{1}H NMR. Compounds (*E*)-**2**, (*Z*)-**2** and **2′** have previously been fully characterized.[13]

20′ (distinguishable peaks in mixture with **2′**): ^{1}H NMR ($CDCl_3$) δ 6.05 (dd, *J* = 17.2, 10.7 Hz, 1 H, CH_2=C*H*), 5.37 (d, *J* = 17.2 Hz, 1 H, trans in CH_2=CH), 5.22 (d, *J* = 10.7 Hz, 1 H, cis in CH_2=CH), 4.23 (br s, 2 H, CH_2OAc), 2.11 (s, 3 H, OAc), 1.68 (s, 3 H, CH_3—C).

20: ^{1}H NMR ($CDCl_3$) δ 5.65 (br t, *J* = 8 Hz, 1 H, C*H*=C), 4.63 (s, 2 H, CH_2OAc), 4.15 (d, *J* = 8 Hz, 2 H, CH_2Cl), 2.08 (s, 3 H, OAc), 1.83 (br s, 3 H, CH_3—C=C).

(*Z*)-1-Acetoxy-4-chloro-2,3-dimethyl-2-butene ((*Z*)-3) was prepared from 2,3-dimethylbutadiene by method A (44%), 20 (0) h, or method B (45%), 32 (28) h. Bulb-to-bulb distillation (100 °C, 1 mmHg) of the crude product afforded **3** consisting of (*Z*)-**3** (83%), (*E*)-**3** (8%),[54] and 4-acetoxy-3-chloro-2,3-dimethyl-1-butene (**3′**) (9%) according to ^{1}H NMR analysis.

(*Z*)-**3**: ^{1}H NMR ($CDCl_3$) δ 4.64 (s, 2 H, CH_2OAc), 4.17 (s, 2 H, CH_2Cl), 2.08 (s, 3 H, OAc), 1.84 (s, 3 H, CH_3 β to Cl), 1.78 (s, 3 H, CH_3 β to OAc); (C_6D_6) δ 4.45 (s, 2 H, CH_2OAc), 3.87 (s, 2 H, CH_2Cl), 1.64 (s, 3 H, OAc), 1.50 (s, 3 H, CH_3 β to Cl), 1.46 (s, 3 H, CH_3 β to OAc); ^{13}C NMR ($CDCl_3$) δ 170.9 (s, CH_3*C*OO), 131.6 (s), 130.3 (s), 64.30 (t, *C*H_2OAc), 45.45 (t, *C*H_2Cl), 20.92 (q, *C*H_3COO), 17.59 (q), 17.53 (q).

(*E*)-**3** (distinguishable peaks in mixture with (*Z*)-**3**): ^{1}H NMR ($CDCl_3$) δ 4.61 (s, 2 H, CH_2OAc), 4.10 (s, 2 H, CH_2Cl); (C_6D_6) δ 4.39 (s, 2 H, CH_2OAc), 3.62 (s, 2 H, CH_2Cl).

Treatment of **3** with the shift reagent Eu(fod)$_3$ revealed information about the double bond configuration. Thus, the methylene protons are more shifted for the major isomer than for the minor isomer, while the reversed is true for the vinylic methyls.

3′ (distinguishable peaks in mixture with (*E*)- and (*Z*)-**3**): ^{1}H NMR ($CDCl_3$) δ 5.12 (m, 1 H, one of CH_2=C), 5.02 (m, 1 H, one of CH_2=C), 4.4–4.25 (AB spectrum, J_{AB} = 11.5 Hz, 2 H, CH_2OAc), 1.91 (d, *J* = 1.5 Hz, 3 H, CH_3—C=C), 1.60 (s, 3 H, CH_3—C—Cl); ^{13}C NMR ($CDCl_3$) δ 114.1 (t, *C*H_2=C).

For analytical purpose, **3** (0.5 mmol) was converted to 1,4-diacetoxy-2,3-dimethyl-2-butene (**34**) by reaction with KOAc (196 mg, 2 mmol) in Me_2SO (2 mL) at 70 °C for 2 h. After the solution cooled, water (2 mL) was added and the aqueous phase was extracted with pentane (4 × 4 mL). The combined organic phases were washed with water (1 mL) and dried ($MgSO_4$). Evaporation of the solvent afforded 94 mg (89%) of **34** as a mixture of *Z*/*E* isomers (10/1).[54]

(*Z*)-**34**: ^{1}H NMR ($CDCl_3$) δ 4.65 (s, 4 H, CH_2OAc), 2.06 (s, 6 H, OAc), 1.77 (s, 6 H, CH_3).

(*E*)-**34**: ^{1}H NMR ($CDCl_3$) δ 4.62 (s, 4 H, CH_2OAc), 2.08 (s, 6 H, OAc), 1.79 (s, 6 H, CH_3).

4-Acetoxy-1-chloro-2-methyl-2-pentene (4) was prepared from (*E*)-2-methyl-1,3-pentadiene by method B (35%, *E*/*Z* = 2.5), 49 (45) h, containing ≈ 7% of the regioisomer 5-acetoxy-4-chloro-4-methyl-2-pentene (**35**): IR (neat) 2980, 1770, 1450, 1370, 1240, 1050 cm^{-1}. Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42. Found: C, 54.40; H, 7.42.

(*E*)-**4**: ^{1}H NMR ($CDCl_3$) δ 5.55 (dq, A part of ABX_3 spectrum, J_{AB} = 8, J_{AX} = 6.1 Hz, 1 H, CH_3—C*H*(OAc)—CH=C), 5.51 (br d, B part of ABX_3 spectrum, J_{AB} = 8, J_{BX} = 0 Hz, CH_3CH(OAc)—C*H*=C), 3.99 (s, 2 H, CH_2Cl), 2.03 (s, 3 H, OAc), 1.83 (d, *J* = 1.2 Hz, 3 H, CH_3—C=C), 1.29 (d, J_{AX} = 6.1 Hz, 3 H, CH_3CHO); ^{13}C NMR ($CDCl_3$) δ 170.2 (s, CH_3*C*OO), 134.8 (s, *C*=CH), 129.5 (d, C=*C*H), 67.52 (d, *C*HOAc), 50.99 (t, *C*H_2Cl), 21.27 (q, *C*H_3C), 20.36 (q, *C*H_3COO), 14.73 (q, *C*H_3—C=C); HPLC, V_r/V_o = 2.6 (EtOAc/hexane = 4/96).

(*Z*)-**4**: ^{1}H NMR ($CDCl_3$) δ 5.61 (dq, A part of ABX_3 spectrum, J_{AB} = 9, J_{AX} = 6.2 Hz, 1 H, CH_3—C*H*(OAc)—CH=C), 5.35 (br d, B part of ABX_3 spectrum, J_{AB} = 9, J_{BX} = 0 Hz, 1 H, CH_3CH(OAc)—C*H*=C), 4.36 (d, *J* = 11 Hz, 1 H, one of CH_2Cl), 3.94 (d, *J* = 11 Hz, 1 H, one of CH_2Cl), 2.02 (s, 3 H, OAc), 1.86 (d, *J* = 1.4 Hz, 3 H, CH_3—C=C), 1.31 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.2 (s, CH_3*C*OO), 135 (s, *C*=CH), 130.1 (d, C=*C*H), 66.95 (d, *C*HOAc), 43.12 (t, *C*H_2Cl), 21.65 (q, *C*H_3—C=C), 20.78 (q, *C*H_3COO), 20.55 (q, *C*H_3CH(OAc)); HPLC, V_r/V_o = 2.3 (EtOAc/hexane = 4/96).

35 (distinguishable peaks in mixture with **4**): ^{1}H NMR ($CDCl_3$) δ 4.56 (s, 2 H, CH_2OAc).

Mixture of 5a and 5b was prepared from (*E*)-1,3-pentadiene or (*Z*)-1,3-pentadiene by method B (51%), 20 (16) h. The ratio **5a**/**5b** = 1.5 was established by ^{1}H NMR.

5a: ^{1}H NMR ($CDCl_3$) δ 5.9–5.8 (m, *J* = 15.6 Hz, 2 H, CH=CH), 5.38 (quin, *J* = 6 Hz, 1 H, C*H*OAc), 4.05 (d, *J* = 6 Hz, 2 H, CH_2Cl), 2.05 (s, 3 H, OAc), 1.33 (d, *J* = 6.5 Hz, 3 H, CH_3CHOAc); ^{13}C NMR ($CDCl_3$) δ 170.1 (s, O*C*OCH$_3$), 133.9 (d, ClCH$_2$—*C*H=CH), 127.8 (d, CH=*C*H—CHOAc), 69.62 (d, *C*HOAc), 44.05 (t, *C*H_2Cl), 21.24 (q, OCO*C*H$_3$), 19.99 (q, *C*H_3CHOAc).

5b: ^{1}H NMR ($CDCl_3$) δ 5.9–5.8 (m, 2 H, *H*C=C*H*), 4.65 (quin, *J* = 6.5 Hz, 1 H, C*H*Cl), 4.58 (d, *J* = 4.8 Hz, 2 H, CH_2OAc), 2.09 (s, 3 H, OAc), 1.61 (d, *J* = 6.7 Hz, 3 H, CH_3CHCl); ^{13}C NMR ($CDCl_3$) 170.1 (s, O*C*OCH$_3$), 135.7 (d, ClCH—*C*H=CH), 127.4 (d, AcOCH$_2$—*C*H=CH), 63.65 (t, *C*H$_2$OAc), 56.54 (d, *C*HCl), 24.90 (q, *C*H$_3$CHCl), 20.87 (q, OCO*C*H$_3$).

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found (for the mixture **5a** and **5b**): C, 51.78; H, 6.68. IR (neat) 2980, 1730, 1440, 1370, 1230, 1140, 1040, 960, 910 cm^{-1}.

Mixture of 6a and 6b was prepared from (*E*)-6-phenyl-1,3-hexadiene (1.7 mmol) by method B (36%), 21 (14) h. After the usual extraction procedure, the combined organic phases were washed with saturated aqueous Na_2CO_3 (2 × 5 mL) and 2 M NaOH (5 mL) and then stirred for 1.5 h with 2 M NaOH (5 mL) which was saturated with $NaBH_4$. In this way the quinoid Diels–Alder adduct was reduced according to HPLC, V_r/V_o = 2.6 (EtOAc/hexane = 2.5/97.5). The organic phase was washed with brine (3 mL), dried ($MgSO_4$), and eluted through a silica column (5 × 2 cm) with EtOAc/hexane (1/1). Evaporation of the solvent afforded 155 mg (36%) of **6** consisting of **6a** (44%), **6b** (43%), and 1-acetoxy-2-chloro-6-phenyl-3-hexene (**6′**) (13%). For analytical purposes, **6a** and **6b** were separated by preparative HPLC.

6a: HPLC, V_r/V_o = 2.8 (EtOAc/hexane = 2.5/97.5); ^{1}H NMR ($CDCl_3$) δ 7.35–7.1 (m, 5 H, Ph), 5.86 (dt, *J* = 15.2 and 5.4 Hz, 1 H, ClCH$_2$—C*H*=CH), 5.77 (dd, *J* = 15.2 and 5.4 Hz, 1 H, CH=C*H*—CHOAc), 5.29 (br q, *J* = 6 Hz, 1 H, C*H*OAc), 4.05 (d, *J* = 5.4 Hz, 2 H, CH_2Cl), 2.65 (t, *J* = 7.3 Hz, 2 H, CH_2Ph), 2.06 (s, 3 H, OAc), 1.97 (br q, *J* = 8 Hz, 2 H, CH_2CH$_2$Ph); ^{13}C NMR ($CDCl_3$) (assigned peaks in mixture with **6b**) δ 72.85 (d, *C*HOAc), 43.96 (t, *C*H_2Cl).

6b: HPLC, V_r/V_o = 3.0 (EtOAc/hexane = 2.5/97.5); ^{1}H NMR ($CDCl_3$) δ 7.35–7.1 (m, 5 H, Ph), 5.95–5.7 (m, 2 H, C*H*=C*H*), 4.57 (d, *J* = 4.5 Hz, 2 H, CH_2OAc), 4.35 (br q, *J* = 6.7 Hz, 1 H, C*H*Cl), 2.80–2.75 (AB part of ABX_2, J_{AB} = 14, J_{AX} = 7 Hz, 2 H, CH$_2$CH_2Ph), 2.12 (br q, *J* = 7 Hz, 2 H CH_2Ph), 2.08 (s, 3 H, OAc),^{13}C NMR ($CDCl_3$) (assigned peaks in mixture with **6a**) δ 60.63 (t, *C*H$_2$OAc), 60.76 (d, *C*HCl).

6′: HPLC, V_r/V_o = 2.4 (EtOAc/hexane = 2.5/97.5); ^{1}H NMR ($CDCl_3$) (distinguishable peaks in mixture with **6a** and **6b**) δ 4.2 (AB part of ABX, 2 H, CH_2OAc), 2.45–2.30 (m, 2 H, CH=CH—CH_2).

Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found (for the mixture **6a**, **6b**, and **6′**): C, 66.65; H, 6.76. IR (neat) 3020, 2920, 1740, 1370, 1230, 1025, 965, 750, 700 cm^{-1}.

Mixture of 7a and 7b was prepared from ethyl (*E*)-4,6-heptadienoate (2 mmol) by method B (58%), 42 (40) h. A slightly modified workup procedure was used. After addition of brine (6 mL) to the reaction mixture, the aqueous phase was extracted with ether/pentane = 40/60 (4 × 20 mL). The combined organic phase was washed with H_2O (2 mL which was saturated with solid K_2CO_3 in the separating funnel) and 2 M NaOH (2 mL). The organic phase was stirred with 2 M NaOH (5 mL saturated with $NaBH_4$) until the Diels–Alder adduct HPLC peak (V_r/V_o = 2, EtOAc/hexane = 10/90) had disappeared (1 h). After washing with 2 M NaOH (2 mL) and brine (5 mL), the organic phase was dried ($MgSO_4$) and the solvents were evaporated, yielding 278 mg (58%) of **7** consisting of **7a** (44%), **7b** (36%), 1-acetoxy-2-chloro-6-carbethoxy-3-hexene (**7′**) (11%), and an unidentified compound (9%) (HPLC V_r/V_o = 2.9). The composition was determined by HPLC and ^{1}H NMR of the mixture.

7a: HPLC, V_r/V_o = 3.3 (EtOAc/hexane = 10/90); ^{1}H NMR (CDCl$_3$) δ 5.84 (dt, *J* = 15.6, 6 Hz, 1 H, ClCH$_2$—C*H*=CH), 5.75 (dd, *J* = 15.6, 6.2 Hz, 1 H, CH=C*H*—CHOAc), 5.31 (br q, *J* = 6.2 Hz, 1 H, C*H*OAc), 4.34 (q, *J* = 7.2 Hz, 2 H, OCH_2), 4.04 (d, *J* = 6 Hz, 2 H, CH_2Cl), 2.35 (t, *J* = 7.3 Hz, 2 H, CH_2CO), 2.08 (s, 3 H, OAc), 1.98 (d, *J* = 6–7 Hz, 2 H, AcOCHCH_2), 1.26 (t, *J* = 7.2 Hz, 3 H, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$) δ 172.5 (s, *C*OOEt), 170.0 (s, O*C*OCH$_3$), 133.6 (d, ClCH$_2$—*C*H=CH), 127.0 (d, CH—*C*H=CHOAc), 72.30 (d, *C*HOAc), 60.57 (t, O*C*H$_2$CH$_3$), 43.82 (t, *C*H$_2$Cl), 30.98 (t, *C*H$_2$CH$_2$CO), 29.23 (t, *C*H$_2$CO), 21.06 (q, OCO*C*H$_3$), 14.21 (q, OCH$_2$*C*H$_3$).

(54) (a) The 60 MHz-spectra of **3** and **34** have been published but the shifts differ slightly from ours. (b) Ganem, B.; Small, V. R., Jr. *J. Org. Chem.* **1974**, *39*, 3728.

7b: HPLC, V_r/V_o = 3.4 (EtOAc/hexane = 10/90); ^{1}H NMR ($CDCl_3$) δ 5.84 (m, 2 H, CH=CH), 4,58 (d, J = 4 Hz, 2 H, CH_2OAc), 4.46 (m 1 H, CHCl), 4.34 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 2.49 (t, J = 7.5 Hz, 2 H, CH_2CO), 2.1 (m, 2 H, CH_2CH_2CO), 2.08 (s, 3 H, OAc); ^{13}C NMR ($CDCl_3$) δ 172.5 (s, COOEt), 170.0 (s, $OCOCH_3$), 131.9 (d, ClCH—CH=CH), 128.8 (d, CH=CH—CH_2OAc), 63.51 (t, CH_2OAc), 60.57 (t, OCH_2CH_3), 60.57 (d, CHCl), 33.24 (t, CH_2CH_2CO), 29.90 (t, CH_2CO), 20.85 (q, $OCOCH_3$), 14.21 (q, OCH_2CH_3).

7′: HPLC, V_r/V_o = 3.1 (EtOAc/hexane = 10/90); ^{1}H NMR ($CDCl_3$) (distinguishable peaks in mixture with **7a** and **7b**) δ 4.22 (AB part of ABX spectrum, J_{AB} = 11.5, J_{AX} = 6, J_{BX} = 7 Hz, 2 H, $ClCHCH_2OAc$); ^{13}C NMR ($CDCl_3$) (distinguishable peaks in mixture with **7a** and **7b**) δ 131.4 (d, ClCH—CH=CH), 127.8 (d, CH=CH—CH_2), 66.95 (t, CH_2OAc), 58.5 (d, CHCl), 33.4 (t), 27.35 (t).

Anal. Calcd for $C_{11}H_{17}ClO_4$: C, 53.12; H, 6.89. Found (for a mixture of **7a** and **7b** which was obtained by preparative HPLC): C, 53.30; H, 6.93. IR (neat) 2940, 1735, 1370, 1230, 1025, 970 cm^{-1}.

***(E)*-(*R*,R**)-2-Acetoxy-5-chloro-3-hexene ((*R*,R**)-10)** was prepared from (*E,E*)-2,4-hexadiene (4 mmol) by method A (55%), 24 (18) h, pentane (24 mL)/acetic acid (16 mL). From the ^{1}H NMR spectrum, the diastereomeric purity was established to be >95% *R*,R**. On conversion to the diacetate (see under preparation of **3**) and by subsequent HPLC analysis, it was found that $E/Z \approx 99/1$.

(*R*,R)-10**: ^{1}H NMR ($CDCl_3$) δ 5.82 (dd, J = 15.4, 6.6 Hz, 1 H, CH=CH—CHCl), 5.72 (dd, J = 15.4, 4.9 Hz, 1 H, CH=CH—CHOAc), 5.36 (dq, J = 6.5, 4.9 Hz, 1 H, CHOAc), 4.53 (quin, J = 6.6 Hz, 1 H, CHCl), 2.06 (s, 3 H, OAc), 1.60 (d, J = 6.6 Hz, 3 H, CH_3CHCl), 1.32 (d, J = 6.5 Hz, 3 H, CH_3CHOAc); ^{13}C NMR ($CDCl_3$) δ 170.1 (s, $OCOCH_3$), 133.2 (d, ClCH—CH=CH), 130.8 (d, CH=CH—CHOAc), 69.57 (d, CHOAc), 56.69 (d, CHCl), 24.94 (q, CH_3CHCl), 21.27 (q, $OCOCH_3$), 20.02 (q, CH_3CHOAc). Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42. Found: C, 54.86; H, 7.42.

(*R*,S)-10** was prepared from (*E,Z*)-2,4-hexadiene by method A, 24 (0) h (62%). From the ^{1}H NMR spectrum, the diastereomeric purity was established to be >95% *R*,S**. On conversion to the diacetate (see under preparation of **3**) and by subsequent HPLC analysis, it was found that $E/Z \approx 99/1$.

(*R*,S)-10**: ^{1}H NMR ($CDCl_3$) δ 5.82 (dd, J = 15.4, 6.6 Hz, 1 H, ClCH—CH=CH), 5.71 (dd, J = 15.4, 5.3 Hz, 1 H, CH=CH—CHOAc), 5.37 (dq, J = 6.5, 5.4 Hz, 1 H, CHOAc), 4.53 (quint, J = 6.6 Hz, 1 H, CHCl), 2.06 (s, 3 H, OAc), 1.60 (d, J = 6.6 Hz, 3 H, CH_3CHCl), 1.32 (d, J = 6.5 Hz, 3 H, CH_3CHOAc); ^{13}C NMR ($CDCl_3$) δ 170.0 (s, $OCOCH_3$), 133.4 (d, ClCH—CH=), 130.8 (d, CH=CH—CHOAc), 69.68 (d, CHOAc), 56.77 (d, CHCl), 25.05 (q, CH_3CHCl), 21.25 (q, CH_3CO), 20.02 (q, CH_3CHOAc); IR (neat) 2980, 1725, 1370, 1240, 1040, 965 cm^{-1}. Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42; Cl, 20.07. Found: C, 54.50; H, 7.35; Cl, 19.91.

***cis*-1-Acetoxy-4-chloro-2-cyclohexene (*cis*-11)** was prepared from 1,3-cyclohexadiene by adding small portions (method B) of the diene (0.62 g, 7.7 mmol) over 3 h to an acetic acid (28 mL) solution of $Pd(OAc)_2$ (87 mg 0.39 mmol), LiCl (0.65 g, 15 mmol), $LiOAc{\cdot}2H_2O$ (1.58 g, 15 mmol), and *p*-benzoquinone (1.76 g, 16 mmol). After the solution was stirred for an additional 2 h at room temperature, brine (30 mL) was added. The workup procedure was the same as for *cis*-**12**. Bulb-to-bulb distillation gave 1.19 g (89%) of *cis*-**11** as a colorless oil (>98% cis according to HPLC): HPLC, V_r/V_o = 4.5 (EtOAc/hexane = 2.5/97.5); ^{1}H NMR ($CDCl_3$) δ 5.97 (ddd, J = 10.0, 3.7, and 1.5 Hz, 1 H, CH=CH—CHCl), 5.81 (dd, J = 10, 3 Hz, 1 H, CH=CH—CHOAc), 5.28 (m, 1 H, CHOAc), 4.56 (brq, 1 H, CHCl), 2.2–1.9 (m, 4 H, CH_2—CH_2), 2.08 (s, 3 H, OAc); IR (KBr) 1740, 1378, 1245, 1038, 880 cm^{-1}. Anal. Calcd for $C_8H_{11}ClO_2$: C, 55.02; H, 6.35; Cl, 20.30. Found: C, 55.00; H, 6.30; Cl, 20.16.

***trans*-11** was obtained in a mixture of *cis*-**11** when *p*-benzoquinone was replaced by MnO_2: (isolated by preparative HPLC, EtOAc/hexane = 2.5/97.5); ^{1}H NMR ($CDCl_3$) δ 6.02 (dd, J = 10, 4 Hz, 1 H, CH=CH—CHCl), 5.89 (dd, J = 10, 4 Hz, 1 H, CH=CH—CHOAc), 5.28 (br q, J = 4 Hz, 1 H, CHOAc), 4.60 (br q, 1 H, CHCl), 2.35–1.9 (m, 3 H, three of CH_2—CH_2), 2.05 (s, 3 H, OAc), 1.85–1.7 (m, 1 H, one of CH_2—CH_2).

***cis*-1-Acetoxy-4-chloro-3-methyl-2-cyclohexane (*cis*-12)** was prepared from 2-methyl-1,3-cyclohexadiene by slow addition of the diene (1.38 g, 14.7 mmol) over 3 h to pentane (70 mL) and an acetic acid (45 mL) solution of $Pd(OAc)_2$ (153 mg, 0.68 mmol), LiCl (1.15 g, 27.2 mmol), $LiOAc{\cdot}2H_2O$ (2.77 g, 27.2 mmol), and *p*-benzoquinone (2.94 g, 27.2 mol) (method A). After the solution was stirred at room temperature for 7 h, brine (25 mL) was added and the mixture stirred (15 min) and then filtered. The organic phase was separated and the aqueous phase extracted with ether/pentane (3 × 100 mL, 10/90). The combined organic phases were washed with H_2O (2 × 50 mL), saturated aqueous Na_2CO_3 (50 mL), 2 M NaOH (2 × 40 mL), and brine (50 mL). After drying ($MgSO_4$), the solvent was removed, yielding crude *cis*-**12** which contained 2-methyl-1,3-cyclohexadiene (≈10%) and the Diels–Alder adduct (≈5%) (δ 3.2–2.9) according to ^{1}H NMR. Bulb-to-bulb distillation gave 1.51 g (55%) of *cis*-**12** (>97% cis according to HPLC): IR (neat) 2950, 1735, 1440, 1360, 1240, 1030, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.53 (br s, 1 H, olefin), 5.29 (br t, J = 7 Hz, 1 H, CHOAc), 4.36 (br t, J = 3–4 Hz, CHCl), 2.25–1.9 (m, 4 H, CH_2—CH_2), 2.07 (s, 3 H, OAc), 1.84 (s, 3 H, CH_3—C=C). Irradiation of CH_2CH_2 afforded $J_{(\text{olefin-}CHOAc)}$ = 3.8 Hz: ^{13}C NMR ($CDCl_3$) δ 170.7 (s, $OCOCH_3$), 138.0 (s, C=CH), 125.9 (d, C=CH), 69.40 (d, CHOAc), 58.11 (d, CHCl), 30.47 (t, CH_2CHCl), 23.43 (t, CH_2CHOAc), 21.23 (q, CH_3C=C), 21.14 (q, $OCOCH_3$); HPLC, V_r/V_o = 2.3 (EtOAc/hexane = 5/95). Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.30; H, 6.95. Found: C, 57.13; H, 6.91.

***trans*-12** (isolated by prepatative HPLC, V_r/V_o = 2.0 (EtOAc/hexane = 5/95)): ^{1}H NMR ($CDCl_3$) δ 5.67 (dt, J = 5, 1.5 Hz, 1 H, olefin), 5.23 (m, 1 H, CHOAc), 4.36 (t, J = 3–4 Hz, 1 H, CHCl), 2.30–1.95 (m, 4 H, CH_2CH_2), 2.03 (s, 3 H, OAc), 1.87 (s, 3 H, CH_3C=C). Irradiation of CH_2CH_2 afforded $J_{(\text{olefin-}CHOAc)}$ = 5.0 Hz.

Mixture of 1β-acetoxy-4β-chloro-6β-methyl-2-cyclohexene (13) and 1β-acetoxy-4α-chloro-5β-methyl-2-cyclohexene (14) was prepared from 5-methyl-1,3-cyclohexadiene by method B, 4.5 (0.5) h, using 7.5 mol % $Pd(OAc)_2$. The yield was 65% consisting of **13** (46%), α-CH_3-**13** (11%), **14** (35%), and β-CH_3-**14** (8%). The composition was determined by integration of CHOAc, CHCl, and CH_3 signals in the ^{1}H NMR spectrum of the mixture. ^{1}H NMR ($CDCl_3$) (overlapping signals) 6.1–5.7 (m, 2 H, olefin), 2.2–1.6 (m, 3 H, CH–CH_2). Distinguishable signals are as follows.

13: ^{1}H NMR ($CDCl_3$) δ 5.38 (br t, J = 8 Hz, 1 H, CHOAc), 4.4 (br s, 1 H, CHCl), 2.07 (s, 3 H, OAc), 1.12 (d, J = 6.6 Hz, 3 H, CH_3CH). α-CH_3-**13**: δ 5.23 (br q, J = 4 Hz, 1 H, CHOAc), 4.11 (br d, J = 10 Hz, 1 H, CHCl), 1.16 (d, J = 6.6 Hz, 3 H, CH_3CH).

14: ^{1}H NMR ($CDCl_3$) δ 5.04 (br d, J = 10 Hz, 1 H, CHOAc), 4.61 (br s, 1 H, CHCl), 2.11 (s, 3 H, OAc), 1.02 (d, J = 6.6 Hz, 3 H, CH_3CH). β-CH_3-**14**: δ 5.12 (br s, 1 H, CHOAc), 4.55 (br d, J = 10 Hz, 1 H, CHCl), 0.99 (d, concealed, CH_3CH).

***cis*-1-Acetoxy-4-chloro-2-cycloheptene (15)** was prepared from 1,3-cycloheptadiene by addition of the diene (683 mg, 7.3 mmol) in one portion to the acetic acid solution (method B), 74%, 12 (0) h. **15** (>98% cis according to ^{1}H NMR): IR (KBr) 1742, 1374, 1245, 1032 cm^{-1}. HPLC V_r/V_o = 2.1 (EtOAc/hexane = 5/95); ^{1}H NMR ($CDCl_3$) δ 5.9–5.6 (m, 2 H, olefinic), 5.38 (m, 1 H, CHOAc), 4.63 (m, 1 H, CHCl), 2.06 (s, 3 H, OAc), 2.2–1.7 (m, 6 H, $(CH_2)_3$); ^{13}C NMR ($CDCl_3$) δ 170.0 (s, $OCOCH_3$), 133.8 (d), 133.4 (d), 72.64 (d, CHOAc), 58.54 (d, CHCl), 36.17 (t, CH_2CHCl), 32.15 (t), 22.80, (t), 21.15 (q, $OCOCH_3$). Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.30; H, 6.95. Found: C, 58.21; H, 6.48.

1β,6α-Diacetoxy-4β-chloro-2-cycloheptene (16) was prepared from 6-acetoxy-1,3-cycloheptadiene by addition of the diene in one portion to the acetic acid solution (method B), 58%, 72 (0) h. **16** (>95% β,β,α according to ^{1}H NMR): IR (neat) 2940, 1735, 1435, 1370 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.91 (br d, 1 H, J = 18 Hz, ClCH—CH=CH), 5.77 (br d, 1 H, J = 12 Hz, CH=CH—CHOAc), 5.62 (br d, 1 H, J = 11 Hz, CH—OAc allylic), 5.36 (dq, 1 H, J = 7, 4.5 Hz, 1 H, CHOAc), 4.83 (m, 1 H, CHCl), 4–2.0 (m, 4 H, CH_2), 2.11 (s, 3 H, OAc), 2.07 (s, 3 H, OAc allylic). Anal. Calcd for $C_{11}H_{15}ClO_4$: C, 53.55; H, 6.13. Found: C, 53.62; H, 6.02.

Mixture of 17 and 17′ was prepared from 1.3-cyclooctadiene by addition of the diene (174 mg, 1.6 mmol) in one portion, 36 (0) h, to an acetic acid (6.5 mL) solution of $Pd(OAc)_2$ (30 mg, 0.16 mmol), $LiOAc{\cdot}2H_2O$ (1.14 g, 11 mmol), LiCl (74 mg, 1.8 mmol), and *p*-benzoquinone (371 mg, 3.4 mmol) (method B). The mixture was stirred for 36 h at 43 °C. Workup gave 256 mg of a crude product, which on bulb-to-bulb distillation afforded 198 mg (61%) of **17** (75%) and **17′** (25%): IR (KBr) 1742, 1372, 1248, 1032 cm^{-1}.

17: ^{1}H NMR ($CDCl_3$) δ 5.8–5.5 (m, 2 H, CH=CH—CHOAc), 4.76 (ddd, J = 12.0, 7.5, 4.5 Hz, 1 H, CHCl), 2.05 (s, 3 H, OAc), 2.2–1.5 (m, 8 H, $(CH_2)_4$).

17′: ^{1}H ($CDCl_3$) δ 5.8–5.5 (m, 2 H, CH=CH), 5.27 (m, 1 H, CHOAc), 4.93 (ddd, J = 8, 3, 1 Hz, 1 H, CHCl), 2.09 (s, 3 H, OAc), 2.1–1.5 (m, 8 H, $(CH_2)_4$).

1β,6α-Diacetoxy-4β-(dimethylamino)-2-cycloheptene (18). **16** (50 mg, 0.2 mmol) in THF (1 mL) was added to $Pd(acac)_2$ (4 mg, 0.013 mmol) and PPh_3 (13.6 mg, 0.052 mmol) in THF (1 mL) under an N_2 atmosphere. Dimethylamine in THF (0.72 mL, 2 M, 1.43 mmol) was added, and the reaction mixture was stirred at 20 °C for 2.5 h. The same workup procedure as described for (*R*,R**)-**21a** from (*R*,R**)-**10** afforded 41 mg (81%) of **18**: ^{1}H NMR ($CDCl_3$) δ 5.94 (br d, J = 11.5 Hz, 1 H, NCH—CH=CH), 5.76 (br d, J = 11.5 Hz, 1 H, AcOCH—CH=CH), 5.65 (br d, J = 10 Hz, 1 H, CHOAc allylic), 5.35 (tt, J =

5.5, 2.5 Hz, 1 H, CHOAc), 3.55 (br d, J = 10 Hz, 1 H, C*H*N), 2.25 (s, 6 H, $(CH_3)_2N$), 2.10 (s, 3 H, OAc) 2.05 (s, 3 H, OAc allylic), 2.1–1.8 (m, 4 H, CH_2).

1β,6α-Diacetoxy-4α-(dimethylamino)-2-cycloheptene (19). **16** (50 mg, 0.2 mmol), Na_2CO_3 (76 mg, 0.72 mmol), dimethylamine (180 mg, 4 mmol), and acetonitrile (5 mL) were heated under reflux (2 days). After filtration and concentration, saturated aqueous Na_2CO_3 (3 mL) was added and the resulting mixture extracted with ether (4 × 4 mL). Drying (K_2CO_3) and evaporation in vacuo (aspirator and then oil pump) afforded 35 mg (69%) of **19**. ^{1}H NMR ($CDCl_3$) δ 5.85 (br d, J = 12 Hz, 1 H, NCH—C*H*=CH), 5.75 (br d, J = 12 Hz, 1 H, AcOCH—C*H*=CH), 5.55 (br d, J = 11.2 Hz, 1 H, C*H*OAc allylic), 5.17 (dq, J = 11, 5.5 Hz, 1 H, C*H*OAc), 3.29 (br d, 11.6 Hz, 1 H, C*H*N), 2.25 (s, 6 H, $(CH_3)_2N$), 2.07 (s, 3 H, OAc), 2.065 (s, 3 H, OAc), 2.2–1.9 (m, 4 H, two-CH_2).

Dimethyl (*cis*-4-Acetoxycyclohex-2-en-1-yl)malonate. A solution of sodium dimethyl malonate in THF [5.3 mL of a 0.125 M solution (0.66 mmol) prepared from equimolar amounts of dimethyl malonate and sodium hydride (80% in oil)] was added to a mixture of palladium acetate (3.0 mg, 0.013 mmol), triphenyl phosphine (15.8 mg, 0.060 mmol), and *cis*-1-acetoxy-4-chloro-2-cyclohexene (**11**) (105 mg, 0.603 mmol) under nitrogen at room temperature. After the solution was stirred for 0.5 h at 25 °C, saturated aqueous sodium hydrogen carbonate (6 mL), water (3 mL), and ether (8 mL) were added. The two layers were separated, and the aqueous layer was extracted with ether (4 × 5 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), concentrated to approximately 2 mL, and filtered through a silica gel column. Eluation with ether followed by evaporation of the solvent and removal of the excess dimethyl malonate by bulb-to-bulb distillation furnished 155 mg (95%) of essentially pure dimethyl (*cis*-1-acetoxy-2-cyclohexenyl)malonate (>98% cis): ^{1}H NMR ($CDCl_3$) δ. 5.85 (br s, 2 H, CH=CH), 5.19 (m, 1 H, CHO), 3.76 (s, 6 H, MeOOC), 3.35 (d, J = 9.5 Hz, 1 H, C*H*—COOMe), 2.88 (m, 1 H, C*H*—CH(COOMe)$_2$), 2.04 (s, 3 H, OAc), 1.9–1.5 (m, 4 H, CH_2); IR (neat) 2950, 1740, 1435, 1370, 1330, 1230, 1150, 1120 cm^{-1}.

Dimethyl (*trans*-4-Acetoxycyclohex-2-en-1-yl)malonate. *cis*-1-Acetoxy-4-chloro-2-cyclohexene (**11**) (166 mg, 0.95 mmol) was added under nitrogen to a solution of sodium dimethyl malonate in dry acetonitrile (10 mL of a 0.113 M solution (1.13 mmol) prepared as above followed by removal of the THF in vacuo and replacing it with CH_3CN). The mixture was heated at reflux for 12 h. Sodium hydrogen carbonate (100 mg, 1.2 mmol) was added and after stirring the mixture at room temperature for 2 h, ether (30 mL) was added followed by filtration. The solvent was removed in vacuo to give a light brown oil (270 mg) containing the product together with dimethyl malonate. The excess dimethyl malonate was removed by bulb-to-bulb distillation to give a residue oil, 242 mg (94%) of essentially pure dimethyl (*trans*-4-acetoxy-2-cyclohexenyl)malonate (>98% trans): ^{1}H NMR ($CDCl_3$) δ 5.75 (br s, 2 H, CH=CH), 5.28 (m, 1 H, CHO), 3.75 (s, 6 H, MeOCO), 3.29 (d, J = 9.0 Hz, 1 H, C*H*—COOMe), 2.98 (m, 1 H, C*H*—CH(COOMe)$_2$), 2.06 (s, 3 H, OAc), 2.1–1.5 (m, 4 H, CH_2): IR (neat) 2960, 1740, 1440, 1375, 1250, 1160, 1030 cm^{-1}.

(*E*)-(*R*,R)-2-Acetoxy-5-(diethylamino)-3-hexene ((*R*,R**)-21a) from (*R*,R**)-10.** To a stirred solution of $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in THF (2 mL) under a N_2 atmosphere was added (*R*,R**)-**10** (70 mg, 0.4 mmol) and diethylamine (200 μL, 2 mmol). After the solution was stirred for 2 h at 20 °C, ether (5 mL) and 2 M HCl (4 mL) were added. The organic phase was then separated and extracted with aqueous 0.1 M HCl (4 × 3 mL). After washing with ether (2 mL), the water phase was saturated with solid K_2CO_3 and extracted with ether (4 × 10 mL). The combined organic phases were dried (K_2CO_3) and the solvent was removed to yield 60 mg (70%) of (*R*,R**)-**21a** (>92% *R*,R** according to ^{1}H NMR): ^{1}H NMR ($CDCl_3$) δ 5.69 (dd, J = 15.5, 6.9 Hz, 1 H, NCH—C*H*=CH), 5.55 (dd, J = 15.6, 5.8 Hz, 1 H, AcOCH—C*H*=CH), 5.34 (quin, J = 6.3 Hz, 1 H, C*H*OAc), 3.30 (quin, J = 6.7 Hz, 1 H, CNH), 2.65–2.37 (m, 4 H, CH_2N), 2.04 (s, 3 H, OAc), 1.30 (d, J = 6.4 Hz, 3 H, CH_3CHOAc), 1.11 (d, J = 6.7 Hz, 3 H, CH_3CHN), 1.01 (t, J = 7.1 Hz, 6 H, CH_3CH_2N); IR (KBr) 2970, 2930, 2800, 1740, 1450, 1370, 1240, 1045 cm^{-1}.

(*R*,R)-21a from (*R*,S**)-10.** (*R*,S**)-**10** (70 mg, 0.4 mmol), K_2CO_3 (138 mg, 1 mmol), diethylamine (334 μL, 3.2 mmol), and CH_3CN (1 mL) were heated under reflux for 25 h. Saturated aqueous Na_2CO_3 (1 mL) was added and the mixture extracted with ether (3 × 5 mL). After drying (K_2CO_3) and rotary evaporation, the crude prouct (75 mg) was bulb-to-bulb distilled, affording 70 mg (80%) of (*R*,R**)-**21a** (>90% *R*,R**) according to ^{1}H NMR ($CDCl_3$).

(*E*)-(*R*,S)-2-Acetoxy-5-(diethylamino)-3-hexane ((*R*,S**)-21a) from (*R*,S**)-10.** The same procedure as for the preparation of (*R*,R**)-**21c** from (*R*,R**)-**10** was applied. (*R*,S**)-**10** (70 mg, 0.4 mmol) furnished 60 mg (70%) of (*R*,S**)-**21a** (>92% *R*,S**) according to ^{1}H NMR (vide infra).

Table III.

$AcOCH_2Cr^1{=}CR^2CH_2Cl \rightarrow$

$AcOCH_2CR^1{=}CR^2CH_2SO_2Ph$ (**22**) + $AcOCH_2CR^1(SO_2Ph)CR^2{=}CH_2$ (**36**)

chloroacetate (E/Z)	R^1	R^2	reaction time, h	**22**, yield (E/Z)	**36**, yield
1 (9/1)	H	H	0.5	**a**, 87% (9/1)	**a**, 9%
2 (3.6/1)[a]	H	CH_3	3[b]	**b**, 92% (3/1)[c]	**b**, 6%[d]
3 (1/10)	CH_3	CH_3	8	**c**, 82% (1/10)	c, 12%

[a] Contains 8% of the regioisomer **20**. [b] 1.6 mol % $Pd(PPh_3)_4$ was used. [c] Contaminated with 5% of 1-acetoxy-2-methyl-4-(phenylsulfonyl)-2-butene. For (*E*)-**22b**, see ref 23. [d] Contaminated with 4-acetoxy-3-methyl-3-(phenylsulfonyl)-1-butene.

(*R*,S)-21a from (*R*,R**)-10.** The same procedure as for the preparation of (*R*,R**)-**21a** from (*R*,S**)-**10** was applied. Bulb-to-bulb distillation of the crude product (80 mg) afforded 72 mg (82%) of (*R*,S**)-**21a** (>90% *R*,S** according to ^{1}H NMR): ^{1}H NMR ($CDCl_3$) δ 5.70 (dd, J = 15.7, 6.6 Hz, 1 H, NCH—C*H*=CH), 5.55 (dd, J = 15.6, 5.6 Hz, 1 H, AcOCH—C*H*=CH), 5.35 (quin, J = 6.4 Hz, 1 H, C*H*OAc), 3.29 (quin, J = 6.8 Hz, 1 H, C*H*N), 2.65–2.37 (m, 4 H, CH_2N), 2.04 (s, 3 H, OAc), 1.31 (d, J = 6.4 Hz, 3 H, CH_3CHOAc), 1.12 (d J = 6.7 Hz, 3 H, CH_3CHN), 1.01 (t, J = 7.1 Hz, 6 H, CH_3CH_2N); IR (KBr) 2970, 2930, 2800, 1740, 1450, 1370, 1240, 1040 cm^{-1}.

Dimethyl ((*E*)-(*R,*S**)-5-Acetoxyhex-3-en-2-yl)malonate ((*R**,*S**)-21c) from (*R**,*S**)-10.** The same procedure as for the preparation of dimethyl (*cis*-4-acetoxy-2-cyclohexenyl)malonate was applied starting with (*R**,*S**)-**10** (88 mg, 0.5 mmol). The excess dimethyl malonate was removed by bulb-to-bulb distillation (90 °C, 1 mmHg), and further distillation (150 °C, 1 mmHg) of the residue afforded 108 mg (79%) of (*R**,*S**)-**21c** (>95% *R**,*S**) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.61 (dd, J = 16, 7 Hz, 1 H, olefin), 5.55 (dd, J = 16, 5 Hz, olefin), 5.28 (quin, J = 4.8 Hz, 1 H, C*H*OAc) 3.74 (s, 3 H, one of CH_3O), 3.70 (s, 3 H, one of CH_3O), 3.28 (d, J = 9 Hz, 1 H, $(CH_3OOC)_2CH$), 2.94 (d quin, J = 9, 7 Hz, 1 H, C*H*—CH(COOMe)$_2$), 2.04 (s, 3 H, OAc), 1.26 (d, J = 6.6 Hz, 3 H, CH_3CHOAc), 1.10 (d, J = 6.6 Hz, 3 H, CH_3CHCH).

(*R,*R**)-21c from (*R**,*R**)-10.** The same procedure as for the preparation of (*R**,*S**)-**21c** from (R*,S*)-**10** was applied. (*R**,*R**)-**10** (88 mg, 0.5 mmol) furnished 135 mg (99%) of (*R**,*R**)-**21c** (>95% *R**,*R**): ^{1}H NMR ($CDCl_3$) δ 5.62 (dd, J = 16, 7 Hz, 1 H, olefin), 5.55 (dd, J = 16, 5 Hz, olefin), 5.28 (quin, J = 4.8 Hz, 1 H, C*H*OAc), 3.74 (s, 3 H, one of CH_3O), 3.69 (s, 3 H, one of CH_3O), 3.28 (d, J = 9 Hz, 1 H, $(CH_3OOC)_2CH$), 2.94 (d quin, J = 9, 7 Hz, 1 H, C*H*CH-(COOMe)$_2$), 2.03 (s, 3 H, OAc), 1.27 (d, J = 6.6 Hz, 3 H, CH_3CHOAc), 1.09 (d, J = 7 Hz, 3 H, CH_3CHCH).

(*E*)-(*R,*S**)-2-Acetoxy-5-(phenylsulfonyl)-3-hexene ((*R**,*S**)-21d) from (*R**,*S**)-10.** To a stirred solution of sodium benzene sulfinate (2.62 g, 16 mmol) and $Pd(PPh_3)_4$ (232 mg, 0.2 mmol) in THF (68 mL) under a N_2 atmosphere at 25 °C was added Me_2SO (12 mL, degassed) and (*R**,*S**)-**10** (704 mg, 4 mmol). The mixture was stirred at 50 °C for 2 h and allowed to cool. Water (70 mL) was then added and the mixture extracted with ether (4 × 60 mL). The combined organic phases were washed with water (30 mL) and brine (30 mL) and finally dried ($MgSO_4$). The solvent was removed and the crude product was purified by flash chromatography, yielding 857 mg (76%) of (*R**,*S**)-**21d** (>95% *R**,*S**) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 2 H, ortho in Ph), 7.65–7.45 (m, 3 H, para and meta in Ph), 5.61 (dd, J = 16.0, 8 Hz, 1 H, SCH—C*H*=CH), 5.44 (dd, J = 16.0, 6 Hz, 1 H, AcOCH—C*H*=CH), 5.25 (quin, J = 6 Hz, 1 H, C*H*OAc), 3.68 (quin, J = 7–8 Hz, 1 H, C*H*S). 2.02 (s, 3 H, OAc), 1.46 (d, J = 7, 3 Hz, CH_3CHS), 1.17 (d, J = 6.5 Hz, 3 H, CH_3CHOAc).

(*E*)-(*R,*R**)-2-Acetoxy-5-(phenylsulfonyl)-3-hexene ((*R**,*R**)-21d) from (*R**,*R**)-10.** Applying the same procedure as for the preparation of (*R**,*S**)-**21d** gave a 71% yield of (*R**,*R**)-**21d** (>94% *R**,*R**): ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 2 H, ortho in Ph), 7.65–7.45 (m, 3 H, para and meta in Ph), 5.64 (dd, J = 16.0, 8 Hz, 1 H, S—CH—C*H*=CH), 5.46 (dd, J = 16.0, 6 Hz, 1 H, AcOCH—C*H*=CH), 5.25 (quin, J = 6 Hz, 1 H, C*H*OAc), 3.69 (quin, J = 7.3 Hz. 1 H, SC*H*), 2.03 (s, 3 H. OAc), 1.46 (d, J = 6.9 Hz, 3 H, CH_3CHS), 1.19 (d, J = 6.5 Hz, 3 H, CH_3CHOAc); IR (neat) 2970, 1730, 1445, 1370, 1300, 1240, 1140, 1040, 730, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{18}SO_4$: C, 59.55; H. 6.43. Found: C, 59.64; H, 6.45.

Preparation of 1-Acetoxy-4-(phenylsulfonyl)-2-alkenes (22a–c). Applying the same procedure as for preparation of (*R**,*S**)-**21d**, but at 20 °C using 5 mmol of chloroacetate in THF (27 mL)–Me_2SO (3 mL), gave **22a-c** (Table III).

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Registry No. (*E*)-**1**, 34414-28-3; (*Z*)-**1**, 55613-61-1; **1′**, 96039-67-7; (*E*)-**2**, 24529-80-4; (*Z*)-**2**, 24529-81-5; **2′**, 38872-51-4; (*E*)-**3**, 53060-20-1; (*Z*)-**3**, 95177-48-3; **3′**, 96039-68-8; (*E*)-**4**, 76355-81-2; (*Z*)-**4**, 96039-69-9; **5a**, 82736-36-5; **5b**, 82736-37-6; **6a**, 96039-70-2; **6b**, 96039-71-3; **6′**, 96039-72-4; **7a**, 96039-73-5; **7b**, 96039-74-6; **7′**, 96039-75-7; (*R**,*R**)-**10**, 95177-49-4; (*R**,*S**)-**10**, 95177-50-7; *cis*-**11**, 82736-39-8; *trans*-**11**, 96039-76-8; *cis*-**12**, 96039-77-9; *trans*-**12**, 96039-78-0; **13**, 96039-79-1; α-CH_3-**13**, 96039-80-4; α-CH_3-**14**, 96039-81-5; β-CH_3-**14**, 96039-82-6; **15**, 82736-40-1; **16**, 96039-83-7; **17**, 96039-84-8; **17′**, 96039-85-9; **18**, 96039-86-0; **19**, 96094-31-4; **20**, 58511-44-7; **20′**, 96039-87-1; (*R**,*R**)-**21a**, 96039-88-2; (*R**,*S**)-**21a**, 96039-89-3; (*R**,*R**)-**21c**, 96039-90-6; (*R**,*S**)-**21c**, 96039-91-7; (*R**,*R**)-**21d**, 95177-61-0; (*R**,*S**)-**21d**, 95177-63-2; **22** (R^1 = CH_3; R^2 = H), 53588-14-0; (*E*)-**22a**, 95177-57-4; (*Z*)-**22a**, 95177-58-5; (*E*)-**22b**, 59830-31-8; (*Z*)-**22b**, 89345-64-2; (*E*)-**22c**, 95177-59-6; (*Z*)-**22c**, 95177-60-9; (*E*)-**34**, 3780-51-6; (*Z*)-**34**, 96039-92-8; **35**, 96039-93-9; **36** (R^1 = CH_3; R^2 = H), 96055-48-0; **36a**, 95199-57-8; **36b**, 95199-58-9; **36c**, 95199-59-0; $Pd(PPh_3)_4$, 14221-01-3; $Pd(PhCN)_2Cl_2$, 14220-64-5; CH_2=CHCH=CH_2, 106-99-0; PPh_3, 603-35-0; $Pd(OAc)_2$, 3375-31-3; LiCl, 7447-41-8; LiOAc, 546-89-4; CH_2=$C(CH_3)C(CH_3)$=CH_2, 513-81-5; (*E*)-CH_2=$C(CH_3)CH$=$CHCH_3$, 926-54-5; (*E*)-CH_2=CHCH=$CH(CH_2)_2$Ph, 77605-16-4; (*E*)-CH_2=CHCH=$CH(CH_2)_2$COOEt, 71779-51-6; (*E*,*Z*)-CH_3CH=$CHCH$=$CHCH_3$, 5194-50-3; (*E*,*E*)-CH_3CH=$CHCH$=$CHCH_3$, 5194-51-4; CH_2=$C(CH_3)CH$=CH_2, 78-79-5; (*Z*)-CH_2=$CHCH$=$CHCH_3$, 1574-41-0; (*E*)-CH_2=$CHCH$=$CHCH_3$, 2004-70-8; $Pd(acac)_2$, 14024-61-4; Me_2NH, 124-40-3; Et_2NH, 109-89-7; $CH_2(COOMe)_2$, 108-59-8; $PhSO_2Na$, 873-55-2; 6-acetoxy-1,3-cycloheptadiene, 29207-42-9; 6-hydroxy-1,3-cycloheptadiene, 1121-63-7; 1,3-cyclohexadiene, 592-57-4; 2-methyl-1,3-cyclohexadiene, 1489-57-2; 6-methyl-4a,5,8,8a-tetrahydro-5,8-ethano-1,4-naphthoquinone, 96039-94-0; 5-methyl-1,3-cyclohexadiene, 19656-98-5; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; dimethyl (*cis*-4-acetoxy-2-cyclohexenyl)malonate, 82736-52-5; dimethyl (*trans*-4-acetoxy-2-cyclohexenyl)malonate, 82736-53-6.

Supplementary Material Available: Experimental data on compounds **22** and **36** (2 pages). Ordering information given on any current masthead page.

Synthesis, Thermolysis, and Photolysis of the Azoalkane 4,5-Diazatricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene: Denitrogenation vs. Azirane Formation

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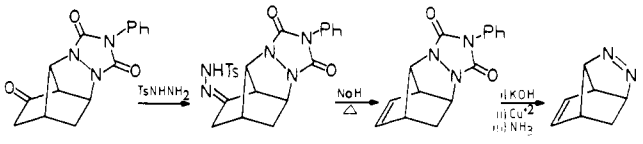
Abstract: The azoalkane 4,5-diazatricyclo[4.3.0.$0^{3,7}$]nona-4,8-diene (**4**) was prepared by reaction of the keto urazole **1** with *p*-toluenesulfonohydrazide, treatment of the hydrazone with sodium hydride, which lead to the corresponding urazole **3**, and subsequent oxidative hydrolysis. Thermolysis of the azoalkane **4** gave mainly (ca. 95%) the retro-Diels–Alder product (*Z*)-pyrazole **7**, which isomerized to the (*E*)-pyrazole **7** and the dihydroindazole **8**. To a small extent (5%) the 1- and 2-vinylcyclopentadienes were produced, presumably via thermolysis of the tricyclo[3.2.0.$0^{2,7}$]hept-3-ene (**5**). In the direct photolysis the tricycloalkene **5** and the azirane **6** were formed in the ratio of ca. 1:1, together with traces of quadricyclane, whereas in the benzophenone-sensitized photolysis the azirane **6** was obtained exclusively. In terms of a Salem diagram it is proposed that in the $^{1,3}n,\pi^*$-excited azoalkane C–C bond cleavage occurs leading to a doubly allyl-stabilized $D_{\pi,\pi}$ diradical, which subsequently cyclizes into the azirane **6**. In the direct photolysis competitive C–N bond cleavage is observed, leading almost exclusively to the tricycloalkene **5** and a little quadricyclane, but no norbornadiene. The 1,3-diradical **12** serves as immediate precursor to the tricycle **5**.

A recent paper[1] on the unusual valence isomerization of perfluoronorbornadiene, involving a thermal di-π-methane rearrangement of quadricyclane into tricyclo[3.2.0.$0^{2,7}$]hept-3-ene presumably via the 1,3-diradical bicyclo[2.2.1]hept-5-ene-2,7-diyl, prompts us to report our results on the latter parent species, generated in the thermolysis and photolysis of 4,5-diazatricyclo-[4.3.0.$0^{3,7}$]nona-4,8-diene (**4**). The synthesis of this new azoalkane commenced with the known keto urazole **1**[2] (eq 1); its details and spectral data are given in the Experimental Section.



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The products of the thermal (vacuum flash pyrolysis or VFP at 350 °C and 20 torr) and direct photochemical (irradiation with the 334-, 351-, and 364-nm lines of an argon ion laser in C_6D_6 or CD_3CN) and triplet sensitized reactions (0.45 M benzophenone in C_6D_6, irradiating only with the 364-nm line of an argon ion laser) are given in Scheme I. The product yields were determined by quantitative ^1H NMR (400 MHz) and/or capillary GC (50-m Carbowax 20 M; injector, column, and detector temperatures of 80, 60 and 120 °C; nitrogen carrier gas pressure 0.25–0.30 kg/cm^2). Product balance was better than 75%, remainder being intractable high-molecular-weight material. The retention times and spectral data of the known volatile products tricycloalkene **5**,[3] norbornadiene, quadricyclane, and mixture of vinylcyclopentadienes[4] were identical with authentic compounds. The

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