Pd^{II}-catalysed Isomerisations of 3-Acetoxy-1,4-dienes to 1-Acetoxy-2,4-dienes: Stereochemical and Preparative Aspects

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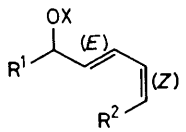
Summary The rapid Pd^{II}-catalysed rearrangement of 3-acetoxy-1,4-dienes to 1-acetoxy-2,4-dienes [*e.g.* (2*E*,5*Z*)-4-acetoxydeca-2,5-diene → (3*E*,5*Z*,)-2-acetoxydeca-3,5-diene (*ca.* 80%)] occurs in a stereoselective and regioselective manner.

THE structural fragment (**1**) occurs in several natural substances or their products of degradation.[1] We have found that this unit can be efficiently generated [*cf.* Table] by the Pd^{II}-catalysed rearrangement of 3-acetoxy-1,4-dienes.[2]



(**1**) X = H, OH, or COR

The scope of this type of reaction was studied with substrates that possess either a vinyl group and a disubstituted double-bond (*E* or *Z*) or two disubstituted double-bonds (all combinations of *E* and *Z*) (*cf.* Table). For such transformations monitored by ^1H n.m.r. spectroscopy in [$^2H_6$]benzene we used as catalyst $(PhCN)_2PdCl_2$ (5 mol %); for preparative experiments, $(MeCN)_2PdCl_2$ (5 mol %) in tetrahydrofuran (THF) was employed. In a typical experiment, to (*E*,*Z*)-4-acetoxyhepta-2,5-diene (0·5 g) in dry THF (5 cm^3) was added $(MeCN)_2PdCl_2$ (42 mg) with stirring. After 5 min at room temperature the solution was evaporated, pentane was added, and the resulting suspension was filtered. The filtrate was concentrated and fractionally distilled (Kugelröhr; b.p. 85—87 °C/2 mmHg) to give an oil (0·46 g, 92%) containing (3*E*,5*Z*)-2-acetoxyhepta-3,5-diene (*ca.* 80%) [δ (CCl_4) 1·30 (d, *J* 6 Hz, *Me*CHOAc), 1·75 (d, *J* 6·5 Hz, *Me*CH=), 1·9 (s, OCO*Me*), 5·3—5·7 (m, 2-, 5-, and 6-H), 5·9 (dd, *J* 10·5 and 10—11 Hz, 3-H), and 6·45 (dd, *J* 10·5 and 15 Hz, 4-H); *m/z* 154 (M^+, 16), 112 (24), 95 (39), 79 (100), and 43 (83); λ_{max} (hexane) 228 nm (ε 23000)] and the (3*E*,5*E*)-isomer (*ca.* 20%) (principally detected by the resonance for 4-H at δ 6·1) [assignments aided by additions of $Eu(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato) and *cf.* ref. 1b].

The results presented show that the Pd^{II}-catalysed isomerisations of 3-acetoxy-1,4-dienes occur preferentially at (*E*)-disubstituted double-bonds. This circumstance is

TABLE. Pd^{II}-catalysed rearrangement of 3-acetoxy-1,4-dienes.[a]

Substrate	Product(s)[b]
(*E*,*E*)-MeCH=CHCH(OAc)CH=CHMe (10 min)	(*E*,*E*)-MeCH=CHCH=CHCH(OAc)Me[c] (*ca.* 100%)
(*Z*,*Z*)-MeCH=CHCH(OAc)CH=CHMe (30 min)	(*Z*,*E*)-MeCH=CHCH=CHCH(OAc)Me (*ca.* 100%)
(*Z*,*E*)-R^1CH=CHCH(OAc)CH=CHR^2 (20 min)	(*Z*,*E*)-R^1CH=CHCH=CHCH(OAc)R^2 (80%) + 20% (*E*,*E*)-isomer(s) (R^1, R^2 = Me, Me[d]; Me, Bu; or Bu, Me)
(*E*)-CH_2=CHCH(OAc)CH=CHMe (30 min)	(*E*)-CH_2=CHCH=CHCH(OAc)Me (≥ 95%)
(*Z*)-CH_2=CHCH(OAc)CH=CHMe (48 h)	(*E*)-CH_2=CHCH=CHCH(OAc)Me (60%) + $AcOCH_2CH$=CHCH=CHMe [30% (*E*,*E*) + 10% (*E*,*Z*)-isomer]

[a] All transformations at room temperature, both in n.m.r. tubes and on a preparative scale (isolated yields > 90%). [b] All new compounds gave ^1H n.m.r., i.r., u.v., and electron impact mass spectra in accord with their assigned structures. [c] Identical with a sample prepared from sorbic aldehyde. [d] Increasing % of (*E*,*E*)-product with longer reaction times.

favourable for synthetic applications because (*i*) (*E*,*Z*)-3-acetoxy-1,4-dienes are easy to prepare from (*E*)-α,β-unsaturated aldehydes *via* (*E*,*Z*)-3-hydroxy-1,4-dienes;[3] they are converted into predominantly (2*E*,4*Z*)-1-acetoxy-2,4-dienes. (*ii*) The preferred direction of allylic rearrangement can be predicted [(*E*,*Z*)-R^1CH=CHCH(OAc)CH=CHR^2 → (*E*,*Z*)-R^1CH(OAc)CH=CHCH=CHR^2].

These points were illustrated with the substrates (2*E*,5*Z*)-4-acetoxydeca-2,5-diene and (2*Z*,5*E*)-4-acetoxydeca-2,5-diene. The (2*E*,5*Z*)-diene [in THF, $(MeCN)_2PdCl_2$ (5 mol %), 10 min] gave an oil (92%) containing (3*E*,5*Z*)-2-acetoxydeca-3,5-diene (*ca.* 80%) and other isomer(s) (*ca.* 20%)† (analysis by ^1H n.m.r. spectroscopy). Hydrogenation (H_2–Pt–THF) of this product gave 2-acetoxydecane (*ca.* 95%) and 5-acetoxydecane (5%) (analysis by g.l.c.). Similarly, (2*Z*,5*E*)-4-acetoxydeca-2,5-diene gave (2*Z*,4*E*)-6-acetoxydeca-2,4-diene (*ca.* 80%) and other isomer(s) (*ca.* 20%).† Hydrogenation of this product gave 5-acetoxydecane (*ca.* 88%) and 2-acetoxydecane (*ca.* 12%).

The reactions described are likely to be mechanistically related to Pd^{II}-catalysed isomerisations of allylic acetates which probably take place *via* an intermediate acetoxonium ion.[4–7] The configuration of the main product is *E*, irrespective of whether the starting material is an (*E*)- or (*Z*)-allylic acetate.[7] It is significant that Pd^0-catalysed rearrangements of 3-acetoxy-1,4-dienes take a quite different stereochemical course from the Pd^{II}-catalysed reactions described. Thus, treatment of either (*E*,*E*)-, (*E*,*Z*)- or (*Z*,*Z*)-4-acetoxyhepta-2,5-diene with $(Ph_3P)_4Pd$ (5 mol %)[8] in benzene gave, within a few minutes at room temperature, (*E*,*E*)-2-acetoxyhepta-3,5-diene (*ca.* 100%). Both (*E*)- and (*Z*)-3-acetoxyhexa-1,4-diene with $(Ph_3P)_4Pd$ (5 mol %) in benzene gave predominantly (> 80%) (*E*,*E*)-1-acetoxyhexa-2,4-diene.

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† The principal by-product appears to be the corresponding (*E*,*E*)-isomer (dd at δ 6·1 for 4-H). *N.B.* (*E*,*E*)-6-acetoxydeca-2,4-diene did not equilibrate with (*E*,*E*)-2-acetoxydeca-3,4-diene when incubated for 30 min at room temperature with $(PhCN)_2PdCl_2$ (5 mol %) in benzene.

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