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REDUCTIVE DISPLACEMENT OF ALLYLIC ACETATES BY HYDRIDE TRANSFER VIA CATALYTIC ACTIVATION BY PALLADIUM(0) COMPLEXES

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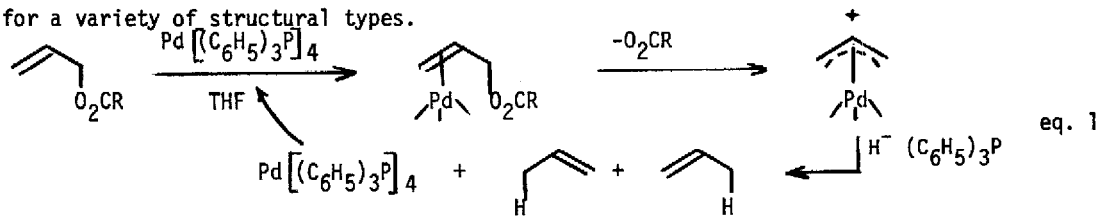
Abstract: Allylic acetates are reduced to alkenes by reductive displacement by hydride reagents via catalytic activation with Pd(0) complexes. In the absence of hydrides, allylic acetates afford conjugated dienes in DMSO solvent.

Under suitable conditions, a number of σ-bonded functional groups are susceptible to nucleophilic displacement by hydride transfer reagents.[1] However, this reductive approach is limited to moieties which not only are relatively good leaving groups toward substitution but also remain inert to other reductive transformations by the reagent (i.e. halogens, sulfonate esters, epoxides, tertiary amines, disulfonimides, etc.).[1] Thus, carbonyl-containing groups such as carboxylates cannot normally be removed by displacement since they are unreactive toward mild hydride transfer reagents (i.e. $NaBH_4$,[1] $NaBH_3CN$[2]) or suffer carbonyl attack by more powerful examples (i.e. $LiAlH_4$,[3] $Li(R_3)BH$[1c]) to afford alcohols.

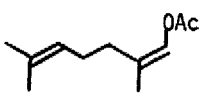
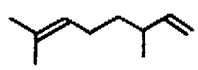
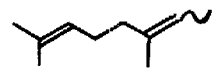
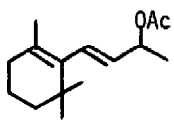
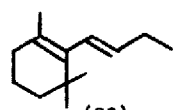
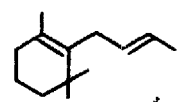
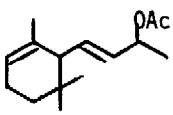
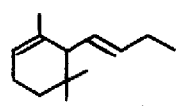
We report a convenient method to circumvent this reluctance toward hydride replacement of carboxylate groups when located at allylic positions. The procedure relies on activation by initial complexation with Pd(0) derivatives[4] followed by carboxylate anion expulsion and subsequent hydride attack on the resulting π-allyl complex as depicted in eq. 1. Both $NaBH_4$ and $NaBH_3CN$ appear to be effective and the process is catalytic in the palladium complex. Table I presents results for a variety of structural types.



eq. 1

The regioselectivity of hydride approach to π-allyl palladium complexes appears to depend on steric and electronic factors. With allylic acetates conjugated to aromatic rings, the corresponding conjugated alkenes are produced almost exclusively (entries 4-9, Table I). However, with aliphatic cases mixtures of regioisomers are obtained depending on the temperature and hydride reagent. For example, 2-decenyl-1-acetate gave a predominance of 2-decene with $NaBH_4$ at ambient

Table I. Reduction of Allylic Acetates to Alkenes

Entry	Acetate[a]	Hydride	Temp °C(T, Hrs)	Products(% Isomers)[k]	% Yield[b]
1	$C_6H_5CH{=}CHCH(OAc)C_6H_5$	$NaBH_3CN$	25 (24)	$C_6H_5CH{=}CHCH_2C_6H_5$	89
2		$NaBH_3CN$	66 (4)		84
3		$NaBH_4$	25 (21)		82
4	$C_6H_5CH{=}CHCH_2OAc$	$NaBH_3CN$	66 (16)	$C_6H_5CH{=}CHCH_3$ (99) $C_6H_5CH_2CH{=}CH_2$ (1)	90
5	$o\text{-}O_2NC_6H_4CH{=}CHCH_2OAc$	$NaBH_3CN$	66 (3)	$o\text{-}O_2NC_6H_4CH{=}CHCH_3$	80
6		$NaBH_3CN$	25 (23)		67
7	$(C_6H_5)_2C{=}CHCH_2OAc$	$NaBH_3CN$	66 (96)	$(C_6H_5)_2C{=}CHCH_3$	78
8		$NaBH_4$	66 (48)		60
9	$C_6H_5CH{=}C(CH_3)CH_2OAc$	$NaBH_4$	66 (2)	$C_6H_5CH{=}C(CH_3)_2$	67
10	$CH_3(CH_2)_6CH{=}CHCH_2OAc$-E	$NaBH_3CN$	25 (24)	$CH_3(CH_2)_6CH{=}CHCH_3$ 46.5)[c] $CH_3(CH_2)_7CH{=}CH_2$ (53.5)	95[l]
11		$NaBH_3CN$	66 (3.5)	$CH_3(CH_2)_6CH{=}CHCH_3$ (54)[d] $CH_3(CH_2)_7CH{=}CH_2$ (46)	87[l]
12		$NaBH_4$	25 (24)	$CH_3(CH_2)_6CH{=}CHCH_3$ (89)[e] $CH_3(CH_2)_7CH{=}CH_2$ (11)	57[l]
13		$NaBH_4$	66 (3.5)	$CH_3(CH_2)_6CH{=}CHCH_3$ (84)[f] $CH_3(CH_2)_7CH{=}CH_2$ (16)	78[l]
14		$NaBH_3CN$	66 (44)	 (59)  (41)[g]	71
15		$NaBH_3CN$	66 (48)	(58) (42)[h]	68
16		$NaBH_3CN$	66 (26)	 (89)  (4)[i]	97
17		$NaBH_3CN$	66 (48)	 (93)[j]	98

(a) Reactions were 0.1 M in the acetate, 0.07 M in $(C_6H_5)_3P$, 0.01 M in $Pd[(C_6H_5)_3P]_4$ and 0.2 M in the hydride reagent in THF. (b) Yields represent isolated, purified products. Ratio of isomers determined by nmr and/or glpc. (c) trans/cis = 3.3:1. (d) trans/cis = 3.5:1. (e) trans/cis = 3:1. (f) trans/cis = 5.2:1.(g) trans/cis = 1.4:1. (h) trans/cis = 1.6:1. (i) Two other unidentified isomers present; ca. 7% of total. (j) Ca. 7% of an unidentified isomer present. (k) stereochemistry of the products not determined unless indicated. (l) Yields determined by glpc.

temperature or in refluxing THF while $NaBH_3CN$ afforded almost random attack at either temperature although the trans/cis ratios varied greatly with all (entries 10-13, Table I). Such dependence of regioselectivity on the nucleophile has been noted in other Pd(0) catalyzed displacements.[4-7] Studies concerning the maintance of stereochemical integrity of the double bond indicate isomerization. Thus, nerol and geranial acetates afforded essentially the same mixture of the 1-, cis-2- and trans-2-alkenes (entries 14,15, Table I) and the alkenes from trans-2-decenyl-1-acetate were likewise isomerized (entries 10-13, Table I). Presumably, this reflects isomerization of the intermediate π-allyl palladium complexes[8] and suggests that hydride transfer by such weak nucleophiles as BH_4^- and BH_3CN^- is slower than interconversion of the π-allylic species.[5]

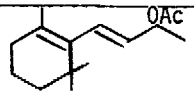
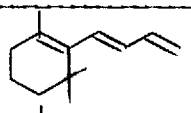
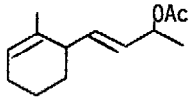
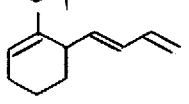
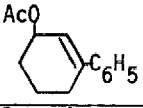
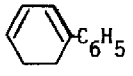
The mildness of $NaBH_3CN$ recommends this reagent where chemoselectivity is important. Thus, o-nitrocinnamyl acetate was converted to 1-(o-nitrophenyl)-propene in good yield (80%) with cyanoborohydride while the corresponding reduction with borohydride gave concomitant reduction of the nitro group and a mixture of products.[9] The fate of other functional groups is currently being explored.[10]

The experimental procedure is straightforward and illustrated for the reduction of 1,3-diphenyl-2-propenyl acetate. A solution of the acetate (756 mg, 3 mmol), $Pd[(C_6H_5)_3P]_4$[11] (345 mg, 0.3 mmol), $(C_6H_5)_3P$ (552 mg, 2.1 mmol) and $NaBH_3CN$ (375 mg, 6 mmol) in 30 ml of dry THF was stirred under argon for 24 hrs at ambient temperature. The yellow solution was then diluted with 2 volumes of saturated NaCl solution and extracted with 3 portions of ether. The ether solution was washed once with saturated $NaHCO_3$, dried ($MgSO_4$) and concentrated. The residue was extracted with 3 portions of pentane, the pentane solution was concentrated and the resulting oil distilled at reduced pressure (Kugelrohr apparatus) to obtain 518 mg (89%) of colorless product which was homogeneous by glpc and identical (nmr) to an authentic sample of 1,3-diphenylpropene.

The reduction of allylic acetates in DMSO at 100°C was attempted in hopes of increasing the rate of hydride deliverance. However, mixtures resulted consisting of substantial quanties of dienes in addition to the alkene reduction products. Evidently, proton abstraction by DMSO competes with reduction. Indeed, in the absence of a hydride reagent, simply heating allylic acetates in DMSO (100°C) gave good to excellent yields of elimination products (Table II)[12] thus providing a convenient method for converting allylic carboxylates to conjugated dienes. Furthermore, the Pd catalyst is readily recovered (80-95%) by cooling the hot DMSO solution after the reaction is complete and filtering the precipitated complex which is then washed with ethanol and ether. The product dienes are obtained from the DMSO by diluting with water and extracting with pentane.

The intermediacy of π-allyl palladium complexes in a variety of reactions from a number of substrates suggests that trapping with hydride reagents may provide fruitful synthetic investigations. We are exploring various possibilities.

Table II. Elimination of Allylic Acetates Catalyzed by Pd(0) in DMSO

Entry	Acetate[a]	Time, Hrs	Product	% Yield[b]
1		14		88
2		14		56
3	cyclododecenyl-3-acetate	22	1,3-cyclododecadiene	72
4		19		42

(a) Reactions were 0.2 M in the acetate, 0.14 M in $(C_6H_5)_3P$ and 0.02 M in $Pd[(C_6H_5)_3P]_4$ in dry DMSO; reaction temperature was 100°C. (b) Yields represent isolated, purified products. Spectral data (nmr, ir) and elemental analyses were consistent with assigned structures.

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