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ASYMMETRIC CATALYTIC ALLYLATION OF β-DIKETONES OR β-KETOESTERS WITH ALLYLIC ETHERS USING A PALLADIUM—DIOP CATALYST: A MECHANISTIC STUDY

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Summary

Allylation of β-diketone, β-ketoesters and methine active hydrogen compounds by allyl phenyl ethers or allyl esters with palladium/phosphine catalytic systems has been studied, and a mechanism is suggested. The use of DIOP (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane) as chiral phosphine ligand produces optically active allylated compounds with up to 10% e.e.

Introduction

Some asymmetric catalytic organic reactions involving chiral coordination complexes have been widely developed, such as hydrogenations or hydrosilylations [1]. Alkylation reactions received less attention, and gave smaller asymmetric inductions. Among the catalysed reactions involving carbon—carbon bond formation, the highest asymmetric inductions reported are in olefin oligomerisation between 1,5-cyclooctadiene and ethylene [2] (88% e.e.), in cyclopropanation [3] (80% e.e.), in hydroformylation [4] (44% e.e.), and more recently in allylic alkylation [5] (up to 45% e.e.).

We report here studies on a system related to allylic alkylation, involving catalytic transfer of an allyl group from an allylic ether or ester to an active hydrogen compound. This reaction was first shown [6] to proceed with methyl acetoacetate to give the monoallylated compound according to eq. 1. Similarly,

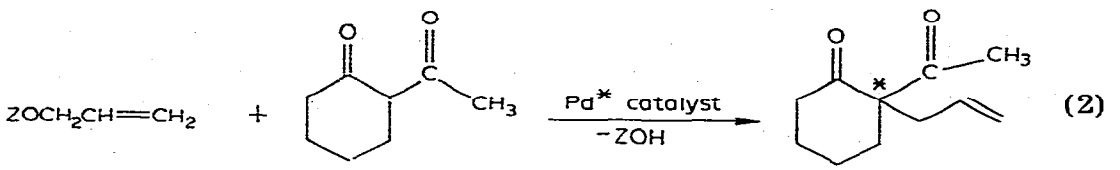
$$PhOCH_2CH{=}CH_2 + CH_3COCH_2CO_2CH_3 \xrightarrow[80^\circ C]{\text{Pd catalyst}} CH_3COCH(CH_2CH{=}CH_2)\,|\,CO_2CH_3 \quad (1)$$

* Dedicated to Professor E. Lederer on the occasion of his 70th birthday.

allylation of acetylacetone with allylic alcohols or allyldiethylamine has been reported [7]. The catalyst used was a mixture of $PdCl_2(PPh_3)_2$ with PhONa as a basic cocatalyst. Few examples of this type of reaction are known, and little information is available on its mechanism.

Scope and mechanistic details

In order to observe asymmetric induction and avoid racemisation in this reaction, we investigated the allylation of methine active compounds leading to quaternary carbon atom. We chose as standard system the allylation of 2-acetylcyclohexanone (II) with allylic ethers or esters I (eq. 2). The catalytic system



(2)

we used was either a palladium(0) complex such as $Pd(dba)_2$ [8] and a chiral phosphine as DIOP (Ib), or a palladium(II) complex such as $PdCl_2$DIOP together with a basic cocatalyst. Optically active III is formed in this reaction (vide infra). Allylation of methyl acetoacetate with allyl phenyl ether takes place at room temperature at a higher rate with (+)DIOP as a ligand in the catalyst than with PPh_3 or dppe.

To define the origin of the asymmetric induction in reaction 2, we needed to know whether the reaction was under kinetic or thermodynamic control. Allyl exchange reaction between alcohols and phenols catalysed by palladium complexes has been shown [6] to be an equilibrium, according to eq. 3.

$$ROC_8H_{13} + PhOH \underset{80^\circ C}{\overset{\text{Pd(II) catalyst}}{\rightleftharpoons}} PhOC_8H_{13} + ROH \qquad (3)$$

(C_8H_{13} = 2,7-octadienyl; R = Me, $PhCH_2$)

We have found that, under these conditions there is no allyl exchange between C-allylated compounds and active methine compounds or phenol. Thus reaction 2 is under kinetic control, because there is no mechanism allowing cleavage of a C-allylic bond.

Results of asymmetric allylation of 2-acetylcyclohexanone by I

In Table 1 are reported results obtained by varying the nature of the reagent in the reaction with II. Alkyl allyl ethers are not allyl donors, allyl acetate is a poor one, and allyl phenyl ether is the best donor.

In runs 2 and 4 of Table 2, the isomeric reagents $PhOCH(CH_3)CH=CH_2$ and $PhOCH_2CH=CHCH_3$ yield an isomeric mixture of the same composition. This means that the reaction probably proceeds via a common intermediate in which the isomeric position of the phenoxy group is lost. This suggests the interven-

TABLE 1

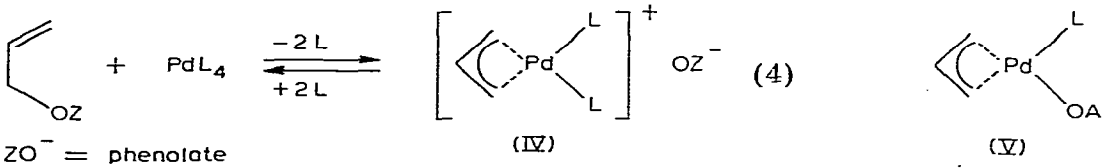
ALLYLATION OF II WITH I [a], I + II → III

I	Yield (%)	$[\alpha]_D^{25}$ ($CHCl_3$, c = 5)
$CH_3OCH_2CH{=}CH_2$	no reaction	
$PhCH_2OCH_2CH{=}CH_2$	no reaction	
$AcOCH_2CH{=}CH_2$	45	+2.0 ± 0.1°
$PhCOCH_2CH{=}CH_2$ [b]	100	+18.0 ± 0.5°

[a] Reaction conditions: 5 mmol I; 5 mmol II; 0.05 mmol $PdCl_2$-(+)DIOP; 0.2 mmol PhONa, no solvent, 60°C, 25 h. [b] Same conditions, except reaction time 4 h at room temperature.

tion of a π-allylic intermediate, the less substituted terminal carbon of which is attacked by the reagent.

The formation of this intermediate may involve the following steps, initiated by catalytic amounts of a palladium(0) complex of PdL_4 type (L being a phosphine). The first step may involve π-complexation of the allylic reagent, and then oxidative addition of the allylic C—O bond on palladium to give the π-allylic complex IV (eq. 4).



ZO^- = phenolate (IV) (V)

The asymmetric carbon atom is formed by nucleophilic addition of the anion (or conjugated base) of the active methylene or methine compound such as II to one of these complexes. In any case, the anion OZ^- is liberated, and used as a base to generate another molecule of enolate A^-. The ambident electrophilic

$$AH + ZO^- \rightleftharpoons A^- + ZOH \qquad (5)$$

cation IV has two sites for reaction: according to HSAB concept [9], hard nucleophiles will preferentially react at palladium (hard center) whereas soft ones will attack the allylic ligand (soft center). The nucleophile (β-diketone and β-ketoester) is also an ambident reagent with both a hard (oxygen atom) and a soft centre (carbon atom). Thus we must consider four different types of primary attack, among which * attack of the allylic ligand by the carbon atom

* Other possible types are:

(a) Attack on the palladium atom by the carbon atom of the enolate ion, followed by a transfer of the new ligand from Pd to the allyl unit. Such transfers are very rare.

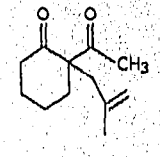
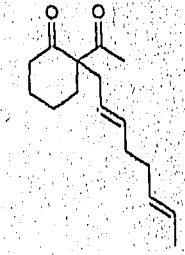
(b) Attack on the palladium atom by the oxygen atom of the enolate, which would probably lead to V by displacement of the chelating phosphine ligand. A related complex π-$C_3H_7Pd(acac)$ has been shown to yield the allylated acetylacetone on heating [10]. This mechanism cannot apply to our case because it is a stoichiometric process.

(c) Attack by the oxygen atom of the enolate ion on the allyl unit of IV, followed by a rearrangement to the C-allylated compound. Such isomerisation of an *O*-allyl vinyl ether has been shown to occur in related systems with platinum catalysts [11,12]. In our case, this possibility can be ruled out because O-allylation would probably occur at the less substituted end of the π-allylic system to give VI as the major product, and this would then isomerise to VII. As IX is the predominant isomer obtained in the reaction (and provided that the rate of the concerted isomerisation of VI to VII is of the same order of magnitude as the rate of cyclisation of VIII to IX), IX must come from C-allylation of the π-allylic system, not from an O-allylation reaction followed by a concerted isomerisation.

We also found that the system $Pd(dba)_2$ + DIOP does not catalyse the rearrangement of X to 2-allylcyclohexanone.

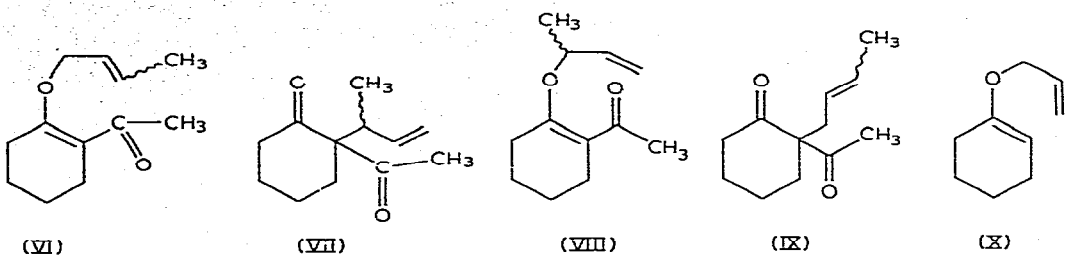
TABLE 2

ALLYLATION OF II WITH ALLYLIC PHENYL ETHERS [a]

Run	Ether	Temperature (°C)	Reaction time (h)	Yield (%)	$[\alpha]_D^{25}$ ($CHCl_3$)	Product
1	$PhOCH_2CH{=}CH_2$	room temperature	4	100	−18.0°	III
2	$PhOCH_2CH{=}CH{-}CH_3$	room temperature	10	90		IX (major) + XII
3	$PhOCH_2C(CH_3){=}CH_2$	50	15	50	+5.0°	
4	$PhOCH(CH_3)CH{=}CH_2$	room temperature	15	50		IX (major) + XII
5	$PhOCH_2CH{=}CH(CH_2)_3CH_2{=}CH$	50	15	95	+6.5°	
6	$PhOCH_2C{\equiv}CH$ [b]	50	15	0		

[a] Reaction conditions: 5 mmol II; 5 mmol allylic phenyl ether; catalytic system: 0.05 mmol $PdCl_2$-(+)DIOP + 0.25 mmol PhONa; no solvent. [b] 3 ml benzene as solvent.

of the enolate ion (C-allylation) is the likely one, leading to formation of a C—C bond, with possible asymmetric induction.



(VI) (VII) (VIII) (IX) (X)

Proposed mechanism for the catalytic allylation

The overall mechanism we propose is depicted in Fig. 1. It involves a catalytic cycle for the palladium and an acid—base reaction for the formation of the enolate. For the catalytic cycle involving the metal, the rate-limiting step is the oxidative addition of the allyl ether. For the acid—base reaction, the stronger the base liberated by the formation of the allylic complex the easier will be the proton abstraction from the active hydrogen compound. If this latter step limits the speed of the overall reaction, the order of reactivity of the reagents would be the same as the order of basicity of the corresponding liberated base, viz. alkyl ethers > allyl phenyl ether > allyl acetate. In fact, allyl alkyl ethers are unreactive (Table 1), indicating that the limiting step lies in the cycle involving the metal. It reflects the ease for oxidative addition of a C—O bond to palladium, following the sequence aryl allyl ether > allyl acetate; this reaction does not take place with alkyl allyl ethers.

The results in Table 3 show that the ease of the reaction, and the sense and the magnitude of asymmetric induction are solvent dependent. In absence of

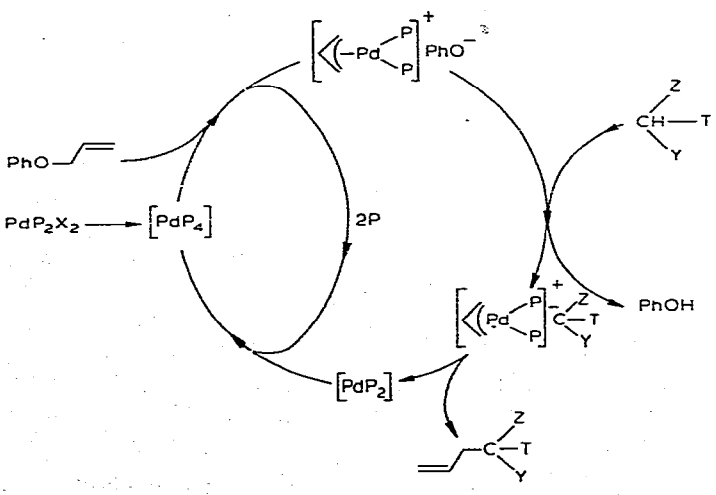


Fig. 1. Mechanism for catalytic allylation.

TABLE 3

SOLVENT INFLUENCE IN THE REACTION I + II → III [a]

Solvent [b]	Reaction time (h)	Yield (%)	$[\alpha]_D^{25}$ ($CHCl_3$, c = 5) of III
Benzene	4	70	+8.0 ± 0.1°
Chloroform	4	100	−11.0 ± 0.5°
THF	15	40	−3.5 ± 0.05°
Dioxane [c]	15	15	—
DME [c]	24	3	—
DMF	15	95	+3.0 ± 0.05°
DMSO	4	95	−0.6 ± 0.01°
Ethanol	15	90	+4.5 ± 0.05°
None	4	100	−18.0 ± 0.1°

[a] 5 mmol I; 5 mmol II; 0.05 mmol $PdCl_2$-(+)DIOP; 0.25 mmol PhONa; room temperature. [b] 3 mL [c] 80°C.

solvent, or with solvents of low polarity and coordinating power (chloroform and benzene), the reaction is faster and there is greater asymmetric induction than with coordinating solvents (dioxane, THF, DME). This may be explained either by saturation of the free coordination sites of complex IV, or by an increase in the concentration of complexes in which the optically active phosphine ligands are replaced by molecules of solvent, giving less reactive achiral complexes.

The question remains of how the palladium(0) complex PdL_4 is formed. It may be produced by an exchange ligand reaction between $Pd(dba)_2$ and DIOP:

$$Pd(dba)_2 + 2\ DIOP \rightarrow Pd(DIOP)_2 + 2\ dba$$

The production of a palladium(0) complex from a palladium(II) complex is less straightforward. Complexes of high oxidation states are reported to be reduced to metal(0) complexes in the presence of bases [13]. Ugo et al. [14] described a route from a palladium(II) to a palladium(0) complex involving reduction by an alcoholate in the presence of a phosphine, according to eq. 6.

$$Pd(PPh_3)_2Cl_2 \xrightarrow{2\ RCH_2O^-} Pd(PPh_3)_2(OCH_2R)_2 \xrightarrow[-2\ RCH_2OH,\ -PPh_3O]{3\ PPh_3,\ H_2O} Pd(PPh_3)_4 \qquad (6)$$

Acetate is probably too weak a base, and would not allow rapid reduction. This mechanism is unlikely in our case, since there is neither excess phosphine present nor water as the proton donating compound, but it could operate if some of the complex were decomposed to give phosphine and metallic palladium, as is often observed with palladium(II) catalytic systems.

For the reaction catalysed by palladium(II) systems we examined especially the influence of the anion and the cation of the cocatalyst on the speed of the reaction, and on the amount of asymmetric induction (Table 4). Surprisingly, the nature of the cation of the cocatalyst can influence the asymmetric induction; in a given reaction, changing PhONa for PhOLi as the cocatalyst of the catalytic system changes the specific optical rotation of product III from −18 to +21, a result difficult to interpret.

The use of optically active salts as cocatalysts for $PdCl_2(dppe)_2$ does not induce any asymmetry in the product. This means that either there is no

TABLE 4

INFLUENCE OF THE COCATALYST ON THE REACTION I + II → III [a]

Cocatalyst	Reaction temperature (°C)	Reaction time (h)	Yield (%)	$[\alpha]_D^{25}$ ($CHCl_3$, c = 5)
PhONa	room	4	100	−18 ± 0.1°
AcONa	80	15	50	+2.4 ± 0.05°
MeONa	room	15	100	+3.3 ± 0.05°
PhOLi	room	1	60	+21 ± 0.1°
$(PhO)_2Ba$	room	1	90	+5 ± 0.05°
[b]	room	1	80	0
[c]	room	24	40	0

[a] Experimental conditions: 5 mmol I; 5 mmol II; 0.05 mmol $PdCl_2$-(+)DIOP (not for *b* and *c*); 0.25 mmol cocatalyst. [b] Disodium salt of (—)-binaphthol [23]. 0.05 mmol $PdCl_2$(dppe). [c] Disodium salt of (+)-2,3-*O*-isopropylidene-L-threitol [24]. 0.05 mmol $PdCl_2$(dppe) as catalyst.

TABLE 5

REACTION I + II → III WITH PALLADIUM(II) CATALYTIC SYSTEMS [a]

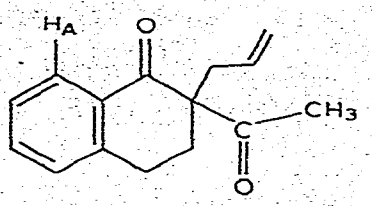
Pd catalyst [b]	Reaction temperature (°C)	Reaction time (h)	Yield (%)	$[\alpha]_D^{25}$ ($CHCl_3$) of III
$PdCl_2$-(+)DIOP + PhONa [c]	room	4	100	−18 ± 0.1°
$Pd(tFAcCam)_2$	60	15	0	
$Pd(tFacCam)_2$ + PhONa [c]	60	15	0	
$Pd(tFacCam)_2$ + dppe [d]	60	15	80	0
$Pd(tFacCam)_2$ + DIOP [e]	room	1	85	+7.1 ± 0.05°

[a] 5 mmol I; 5 mmol II. [b] 0.05 mmol. [c] 0.25 mmol. [d] 0.2 mmol. [e] 0.2 mmol (+)DIOP.

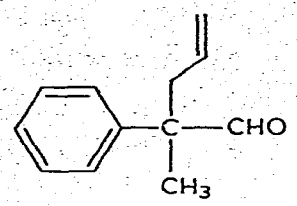
exchange between the phenoxide ion (in IV) and the chiral anion or, if there is, the product causes no induction. If the latter were the case, it could be taken to favour the view that V is probably less efficient than IV for asymmetric induction. $Pd(tFAcCam)_2$ alone or with sodium phenoxide, has no catalytic effect. Addition of an achiral phosphine (dppe) initiates reaction to yield racemic III, while with a chiral phosphine (DIOP), asymmetric induction occurs (Table 5).

Asymmetric syntheses from various substrates

Cyclic β-diketones and β-ketoesters may be cleanly allylated by this process. The products obtained show some optical activity, but since they have never been resolved, their optical purity is difficult to evaluate. We tried to estimate the enantiomeric excess for each compound by PMR spectroscopy in the presence of chiral europium complexes. We separated the vinylic protons in enantiomers of XII (~7% e.e). In benzene at 50°C, 2-acetyl-1-tetralone is allylated into XI $[\alpha]_D^{24}$ − 33.4° (*c* 3, $CHCl_3$); PMR analysis in presence of the chiral shifting reagent $Eu(DCM)_3$ shows two doublets for H_A indicating 10 ± 2% e.e. Even less acidic compounds such as atropaldehyde can be allylated to give 65% XII, $[\alpha]_D^{25}$ − 1.8° (*c* 2, $CHCl_3$) (PMR with $Eu(DCM)_3$ indicates 8% e.e.).



(XI)



(XII)

Conclusion

The reaction we have reported here differs from Trost's allylation [5] of carbanions in that base is present. The asymmetric inductions are lower than in Trost's experiments. This may be explained in terms of the greater distance between the inducing moiety and the developing asymmetric centre. In Trost's system (path a in Fig. 2) the asymmetric carbon atom is formed in the inner coordination sphere, while in our case (provided the nucleophile attacks the face of the π-allyl unit opposite to the palladium [15]) it is formed in the outer coordination sphere (path b).

To provide further understanding of the asymmetric induction from this reaction, we are studying the stereochemistry of the addition of nucleophiles to

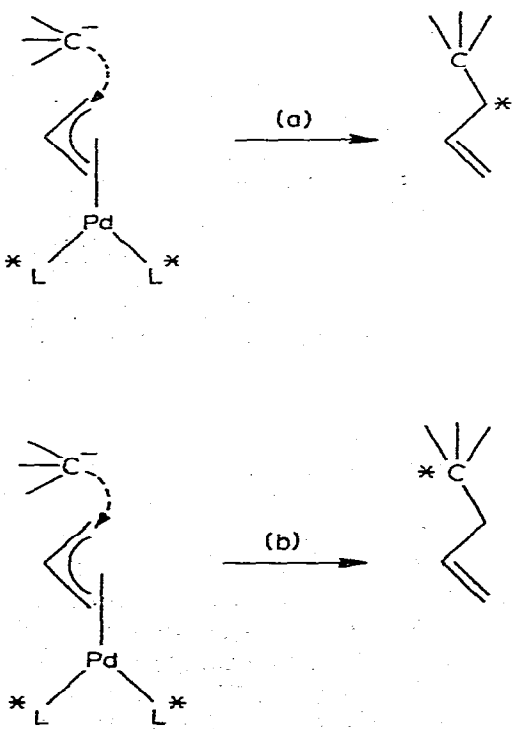


Fig. 2.

π-allylic or olefinic ligands of palladium complexes containing an asymmetric ligand (chiral β-diketone or phosphine). This should help in the choice, for each reaction of a ligand capable of high asymmetric induction.

Experimental

β-Keto esters and β-diketones used throughout this work were purchased from Aldrich and Co. The palladium chloride was a loan from "La Compagnie Française des Métaux Précieux". Phenol salts were made either by treating the metal (Na, Li) with phenol in toluene solution, or by neutralising the phenol with a hydroxide solution ($Ca(OH)_2$, $Ba(OH)_2$). (+)DIOP, prepared from (—)-tartaric acid, showed m.p. 87°C and $[\alpha]_{578}^{25}$ + 12.9° (*c* 2, benzene) [16]. Phenyl allyl ethers were prepared by known procedures [17]. 1-Phenoxy-2,7-octadiene was obtained by treatment of 1,3-butadiene with phenol [18] and $PdCl_2$(dppe) was prepared by Hudson's procedure [19]. Schurig's method for preparation of $Pd(tFAcCam)_2$ was used [20]. $Eu(DCM)_3$ (where DCM represents (+)dicamphorylmethanato) was prepared according to Whitesides' procedure [21]. Optical rotations were measured with a Perkin—Elmer Polarimeter model 141, and infrared spectra with a 257 model. Gas-chromatographic analyses were carried out on a Carlo Erba CGI using a 1.5 m column packed with 15% Apiezon silicon grease on 80/100 mesh Chromosorb W AW, at 170°C. PMR spectra were measured with a R32 Perkin—Elmer Spectrometer (90 MHz); shifts are expressed in δ units (ppm) downfield from tetramethylsilane.

Preparation of $PdCl_2$-(+)DIOP

To a hot solution of 383 mg (1 mmol) dichlorobis(benzonitrile)palladium [22] in 10 ml acetone is added 500 mg (1 mmol) (+)DIOP in 10 ml hot acetone. The yellow solution is heated for 10 minutes (steam bath, 60°C); after cooling, the yellow crystals are filtered off, washed (acetone), and dried, to give 705 mg complex (80% yield). Anal. Found C, 60.61; H, 5.31. $PdCl_2$-(+)DIOP. $C_{31}H_{32}O_2Cl_2Pd$ calcd.: C, 60.65; H, 5.22%.

Allylation of β-keto esters or β-diketones. Standard procedure

A typical reaction was conducted in a Schlenk apparatus, as follows. The reaction was started by placing 5 mmol of allylic compound and 5 mmol of active hydrogen compound in the reaction vessel, replacing air by nitrogen and adding in one portion the catalyst (either 0.05 mmol palladium(0) salt + 0.25 mmol of basic cocatalyst or 0.05 mmol $Pd(dba)_2$ + 0.05 mmol phosphine). The suspension (former case) or the solution (latter case) was stirred for the appropriate time. Aliquots were taken out (syringe), diluted with hexane, washed (water), dried, and submitted to GLC analysis. When the reaction was complete, the mixture was poured into a mixture of hexane and water, the organic layer was washed with dilute (5%) $NaHCO_3$ aqueous solution then water, and dried. The allylated products were purified by silica gel column chromatography, with hexane as eluent.

Allylation of atropaldehyde to XII

A mixture of 1.34 g (10 mmol) atropaldehyde, 1.24 g (10 mmol) 1-phenoxy-

2-propene, 34 mg (0.05 mmol) $PdCl_2$-(+)DIOP and 30 mg (0.25 mmol) sodium phenoxide was stirred under nitrogen for 16 h at 60°C. Work-up as described above gave 1.14 g (65%) 2-methyl-2-phenyl-4-penten-1-al, $[\alpha]_D^{25} = 1.8°$ (*c* 2, $CHCl_3$); PMR with chiral shift reagent $Eu(DCM)_3$/substrate 1/8, CCl_4, integration of methyl singlets of enantiomers indicates 8 ± 2% e.e.

Allylation of 2-acetyl-1-tetralone to XI

0.82 g (5 mmol) 2-acetyl-1-tetralone, 0.75 g (5 mmol) 1-phenoxy-2-propene, 34 mg (0.05 mmol), $PdCl_2$-(+)DIOP and 56 mg (0.5 mmol) sodium phenoxide were stirred for 16 h at 50° C. Treatment and purification on column chromatography yields 0.68 g (68%) XI, $[\alpha]_D^{24} = 33.4$ (*c* 3, $CHCl_3$). PMR (CCl_4), substrate/$Eu(DCM)_3$ 10/1, gives for H_A two separate (18 Hz) broad doublets, integration of which indicates 10 ± 2% e.e. for XI.

PMR data for allylated compounds

2-Acetyl-2-allylcyclohexanone (III): CH_3(s, 3) 2.0; CH_2=C (m, 2) 4.8—5.2; CH=C (m, 1) 5.3—5.7.

2-Acetyl-2-(1-methylallyl)cyclohexanone (VII): CH_3—CO (s, 3) 2.0; CH_3—C (d, 3) 1.1.

2-Acetyl-2-(2-butenyl)cyclohexanone (IX): CH_3—CO (s, 3) 2.1; CH=C (m, 1) 5.1—5.8; CH_3—C (d, 3) 1.65.

2-Methyl-2-phenyl-4-penten-1-al (XII); CH_3 (s, 1) 1.36; CH_2—C (d, 2) 2—6; CH_2=C (m, 2) 4.85—5.15; CH=C (m, 1) 4.8—5.9; CHO (s, 1) 9.4.

2-Acetyl-2-allyl-1-tetralone (XI): CH_3—CO (s, 3) 2.0; H_A (m, 1) 7.9—8.1; other aromatic CH (m, 3) 7.0—7.6.

2-Acetyl-2-(2,7-octadienyl)cyclohexanone: CH_3—CO (s, 3) 1.96; CH vinylic (m, 5) 4.8—6.0.

Acknowledgements

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