N11—C1—N12	116.31 (14)	O11—N11—C1	120.12 (14)
N11—C1—C2	123.88 (14)	O21—N12—O22	121.02 (14)
N12—C1—C2	119.76 (14)	O21—N12—C1	118.58 (13)
N21—C2—N22	118.40 (16)	O22—N12—C1	120.37 (14)
N21—C2—C1	120.83 (16)	C2—N21—H11	121.0 (15)
N22—C2—C1	120.72 (15)	C2—N21—H12	121.1 (15)
O12—N11—O11	120.89 (14)	C2—N22—H21	119.8 (16)
O12—N11—C1	118.91 (14)	C2—N22—H22	121.9 (16)
N11—C1—C2—N21	−4.6 (3)	N12—C1—N11—O11	11.4 (2)
N12—C1—C2—N21	172.89 (15)	C2—C1—N11—O11	−171.03 (15)
N11—C1—C2—N22	177.82 (16)	N11—C1—N12—O21	−148.00 (15)
N12—C1—C2—N22	−4.7 (2)	C2—C1—N12—O21	34.3 (2)
N12—C1—N11—O12	−171.78 (15)	N11—C1—N12—O22	34.1 (2)
C2—C1—N11—O12	5.8 (2)	C2—C1—N12—O22	−143.57 (16)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots$A	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A
N21—H11$\cdots$O11^i	0.88 (2)	2.18 (2)	3.000 (2)	156 (2)
N21—H11$\cdots$O21^{ii}	0.88 (2)	2.50 (2)	3.012 (2)	117.7 (18)
N21—H12$\cdots$O12	0.87 (3)	1.97 (2)	2.608 (2)	128.8 (19)
N21—H12$\cdots$O22^{ii}	0.87 (3)	2.29 (2)	3.009 (2)	140.3 (19)
N22—H21$\cdots$O22^i	0.84 (3)	2.17 (3)	2.901 (2)	146 (2)
N22—H21$\cdots$O11^i	0.84 (3)	2.46 (2)	3.191 (2)	147 (2)
N22—H22$\cdots$O21	0.84 (2)	2.03 (2)	2.636 (2)	128 (2)
N22—H22$\cdots$O12^{iii}	0.84 (2)	2.36 (2)	3.026 (2)	136 (2)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$.

Graphite monochromatized Mo $K\alpha$ radiation was used. Intensity statistics indicated a centrosymmetric space-group symmetry. The selected space group $P2_1/n$ deduced from the systematic extinctions in the diffraction data is further supported by the outcome of the investigation. Preliminary O, N and C positions were obtained by the application of direct methods using the program package *SHELXS*86 (Sheldrick, 1990). The remaining atomic positions were found from subsequent calculations of difference electron-density ($\Delta\rho$) maps. In the final least-squares refinement the H atoms were refined without any positional restraints, but with a common isotropic displacement parameter.

Data collection: *IPDS Software* (Stoe & Cie, 1997). Cell refinement: *IPDS Software*. Data reduction: *IPDS Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL*97.

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(3RS,4RS)-2-Methyl-3,4-diphenyl-5-hexen-3-ol

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Abstract

The minor diastereomer (γ adduct) of the tertiary homoallylic alcohols, formed in the Zn-mediated reaction between 2-methyl-1-phenyl-1-propanone (isobutyrophenone) and 3-chloro-1-phenylpropene (cinnamyl chloride) in tetrahydrofuran/NH_4Cl(aq), was isolated and crystallized. The structure of the title compound, $C_{19}H_{22}O$, confirms that the major and minor diastereomers of the γ adduct formed in the reaction have *syn* and *anti* configurations, respectively.

Comment

Homoallylic alcohols are important synthetic intermediates for the preparation of certain compounds possessing biological activity (Yamamoto, 1987). Homoallylic alcohols are most conveniently prepared by addition of an allylic group to the carbonyl group of an aldehyde or a ketone. This can be accomplished either by addition of an allylic organometallic reagent to the carbonyl compound or by metal-mediated allylation with an allylic halide (Yamamoto, 1993). Methods utilizing aqueous media in metal-assisted allylations have still increased the usefulness of the reaction (Li, 1996).

We have studied the Zn-mediated allylation of aldehydes and unsymmetrical ketones with (E)-3-chloro-1-phenylpropene (cinnamyl chloride) in THF/NH₄Cl(aq) (THF = tetrahydrofuran) (Sjöholm et al., 1994). The main reaction products in the reaction of 2-methyl-1-phenyl-1-propanone (isobutyrophenone) comprised the two diastereomers, (1) (anti) and (2) (syn), of 2-methyl-3,4-diphenyl-5-hexen-3-ol, formed with a diastereomer excess of 24% (for the definition of the terms syn and anti see Sjöholm, 1990). The diastereomers are formed by a mechanism which includes an allylic rearrangement (γ adducts). Small amounts of α adducts formed without allylic rearrangement were also detected (Sjöholm et al., 1994).

(1) anti   (2) syn
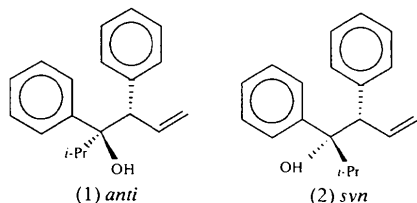
To draw definite conclusions about the detailed reaction mechanisms, the relative configurations at the asymmetric-C atoms of the γ adducts must be known. However, the relative configurations of the diastereomers have been unambiguously established for the benzaldehyde adducts only (Coxon et al., 1991) and were found to be R^*,S^* (anti) for the major isomer.

To elucidate the reaction mechanism in the reactions of ketones we decided to determine the relative configurations of the two stereocentres of the diastereomers from the reaction between 1-phenyl-2-methyl-1-propanone and cinnamyl chloride by determination of the crystal structure of the product using X-ray diffraction. In this reaction the ratio of the γ isomers was 1.6:1 and mainly one α isomer was formed besides the γ isomers. One of the γ isomers crystallized from the mixture and was easily isolated. Analyses by ¹H NMR spectroscopy showed that the isomer which crystallized was the minor one. The X-ray diffraction data showed the minor isomer to have an anti configuration. The relative configuration of the major γ isomer then has to

be syn. Fig. 1 shows a perspective view and the atom labelling of (1). Table 1 lists selected geometric parameters for (1) and the bond parameters are normal.
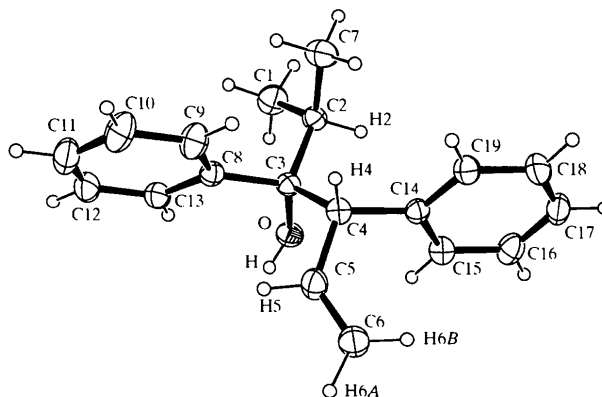

Fig. 1. Perspective view and atom labelling of (1) with displacement ellipsoids drawn at the 30% probability level. Methyl- and aromatic-H atoms are not labelled.

The intramolecular steric interactions are minimized by a staggered conformation at the C3—C4 bond. The benzene rings are antiperiplanar with a C8—C3—C4—C14 torsion angle of −170.1 (2)°. The crystal packing is supported by a weak intermolecular hydrogen bond between the OH groups as indicated by an O···Oⁱ distance of 3.006 (4) Å [symmetry code: (i) 1−x, −y, −z] and the O—H···Oⁱ angle of 166 (3)°.

Experimental

Crystal data

$C_{19}H_{22}O$	Mo $K\alpha$ radiation
$M_r = 266.38$	$\lambda = 0.71069$ Å

Orthorhombic
Pccn
$a = 19.856\,(3)$ Å
$b = 21.450\,(4)$ Å
$c = 7.228\,(5)$ Å
$V = 3078\,(2)$ Å^3
$Z = 8$
$D_x = 1.149$ Mg m^{-3}
D_m not measured

Cell parameters from 25
reflections
$\theta = 13.5{-}18.4°$
$\mu = 0.069$ mm^{-1}
$T = 294\,(2)$ K
Plate
$0.40 \times 0.35 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-5S diffractometer
ω–2θ scans
Absorption correction: none
3126 measured reflections
3126 independent reflections
1635 reflections with
$I > 2\sigma(I)$

$\theta_{max} = 25.00°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 9$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.148$
$S = 1.022$
2713 reflections
199 parameters
H-atom treatment, see below
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.625P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.152$ e Å^{-3}
$\Delta\rho_{min} = -0.218$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O—C3	1.435 (3)	C4—C5	1.511 (4)
O—H	0.771 (16)	C4—C14	1.523 (3)
C1—C2	1.530 (3)	C4—H4	0.97 (3)
C2—C7	1.524 (4)	C5—C6	1.292 (4)
C2—C3	1.553 (3)	C5—H5	0.93 (3)
C2—H2	1.00 (3)	C6—H6A	1.03 (4)
C3—C8	1.544 (3)	C6—H6B	0.97 (3)
C3—C4	1.560 (3)		
C3—O—H	119 (2)	O—C3—C4	107.39 (18)
C7—C2—C1	109.6 (2)	C8—C3—C4	110.59 (18)
C7—C2—C3	113.9 (2)	C2—C3—C4	112.46 (19)
C1—C2—C3	112.6 (2)	C5—C4—C14	112.7 (2)
O—C3—C8	109.74 (18)	C5—C4—C3	110.2 (2)
O—C3—C2	105.18 (18)	C14—C4—C3	114.92 (19)
C8—C3—C2	111.25 (19)	C6—C5—C4	128.9 (3)
O—C3—C4—C5	−58.5 (2)	C8—C3—C4—C14	−170.14 (19)
C8—C3—C4—C5	61.2 (3)	C2—C3—C4—C14	−45.1 (3)
C2—C3—C4—C5	−173.7 (2)	C14—C4—C5—C6	12.1 (4)
O—C3—C4—C14	70.1 (2)	C3—C4—C5—C6	141.9 (3)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O—H⋯O^i	0.771 (16)	2.252 (17)	3.006 (4)	166 (3)

Symmetry code: (i) $1 - x, -y, -z$.

Non-H atoms were refined with anisotropic displacement factors. Methyl- and phenyl-H atoms were included at fixed ideal positions with isotropic displacement parameters ($1.5 \times$ that of the host atom). The rest of the H atoms were refined with fixed isotropic displacement parameters ($1.5 \times$ that of the host atom).

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1995). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: TEXSAN (Molecular Structure Corporation, 1989). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ORTEP-3 for Windows (Farrugia, 1997). Software used to prepare material for publication: SHELXL97.

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4-Hydroxy-2-methyl-N-(5-methyl-1,3-thiazol-2-yl)-2H-1,2-benzothiazine-3-carboxamide 1,1-Dioxide

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Abstract

The thiazine ring in the title compound, $C_{14}H_{13}N_3O_4S_2$, adopts a half-chair conformation. The methyl group at N3 is axial to the thiazine ring due to the tetrahedral