Enantioselective Microbial Reduction of Monoesters of 1,3-Dihydroxypropanone: Synthesis of (*S*)- and (*R*)-1,2-*O*-Isopropylideneglycerol

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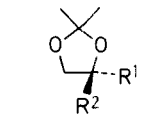
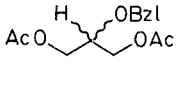
The reduction of 3-benzoyloxy-1-hydroxypropanone with bakers' yeast proceeds enantioselectively to afford (*S*)-3-benzoyloxy-1,2-propanediol, which may be further converted into (*S*)-(benzoyloxymethyl)oxirane. The bioreduction with fermenting yeast of 1-acetoxy-3-benzyloxypropanone gives (*R*)-1-benzyloxy-3-acetoxy-2-propanol which can be used for the preparation of both (*S*)- and (*R*)-1,2-*O*-isopropylideneglycerol.

Chiral 1,2-*O*-isopropylidenglycerols (*R*)-**(1)** and (*S*)-**(1)** and the corresponding aldehydes (*S*)-**(2)** and (*R*)-**(2)** have been used as building blocks for the preparation of enantiomerically pure biologically active compounds such as phospholipids,[1] PAF (platelet aggregation factor),[2] β-blockers,[3] and other compounds.[4] They are usually prepared from D-mannitol [(*S*)-**(1)** and (*R*)-**(2)**][5] and L-serine,[5,6] ascorbic acid,[7] or L-threitol [(*R*)-**(1)** and (*S*)-**(2)**].[8]

Glycerol has for a long time not been considered as an alternative source of chiral building blocks containing the glycerol skeleton. Recently, the enzymatic differentiation of the two enantiotopic groups in the prochiral glycerol derivative 1,3-diacetoxy-2-benzyloxypropane **(3)** was accomplished via selective functional group manipulation.[9]



(*S*)-**1** R^1 = H, R^2 = CH_2OH
(*R*)-**1** R^1 = CH_2OH, R^2 = H
(*S*)-**2** R^1 = CHO, R^2 = H
(*R*)-**2** R^1 = H, R^2 = CHO



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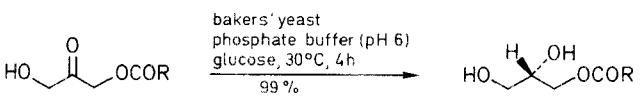
Carbonyl compounds are efficiently reduced by fermenting bakers' yeast in a highly enantioselective manner.[10] The stereochemical outcome of the bioreduction of substituted carbonyl compounds generally follows Prelog's rule.[11] It seemed worthwhile to explore the feasibility of the bioreduction of the monobenzoate or of *Ar*-substituted monobenzoates of 1,3-dihydroxypropanone with bakers' yeast for the enantioselective synthesis of glycerol benzoate. Readily available substrates such as 1-benzoyloxy-3-hydroxypropanone **(4a)** and 3-hydroxy-1-(4-nitrobenzoyloxy)propanone **(4b)** were chosen to introduce a sufficient difference between the substituents around the ketonic group. The use of aliphatic *O*-acyl derivatives was unsuccessful owing to fast microbial hydrolysis.

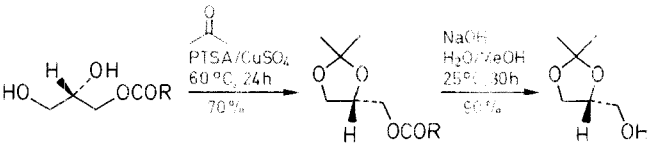


4a,b (*S*)-**5a,b**

4–8	R
a	C_6H_5
b	4-$O_2NC_6H_4$

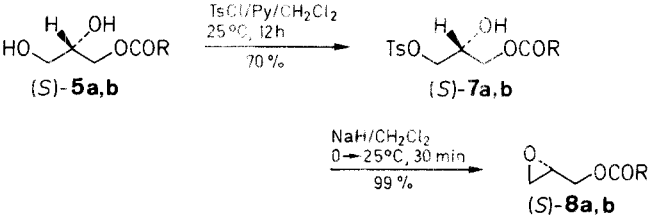
Incubation of ketones **4a** and **4b** with fermenting yeast proceeded satisfactorily and afforded (*S*)-1-benzoyloxy-2,3-propanediol **(5a)** and (*S*)-1-(4-nitrobenzoyloxy)-2,3-propanediol **(5b)**, respectively, in quantitative yield.

The reaction of **5a** and **5b** with (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride[12] afforded the corresponding di-*O*-acyl derivatives in at least 99 % optical purity according to GLC analysis. Thus, the bioreduction of **4a** and **4b** had proceeded according to Prelog's rule, also with high concentrations of substrate (up to 30 g/L), without affecting the optical purity of the product contrary to what had previously been observed for other ketones.[13] Compound **5a** can be transformed into (*R*)-1,2-*O*-isopropylideneglycerol [(*R*)-**1**] via acetal formation with acetone to give 1,3-dioxolane **6a**, followed by hydrolysis of the *O*-benzoyl group.



(*S*)-**5a** (*S*)-**6a** (*R*)-**1**

The conversion of **5a** and **5b** into (*S*)-benzoyloxymethyl **(8a)** and (*S*)-(4-nitrobenzoyloxymethyl)oxirane **(8b)**, respectively, was achieved via reaction of the corresponding tosylates **7a** and **7b** with sodium hydride in dichloromethane no inversion occurring at C-2 under the reaction conditions.

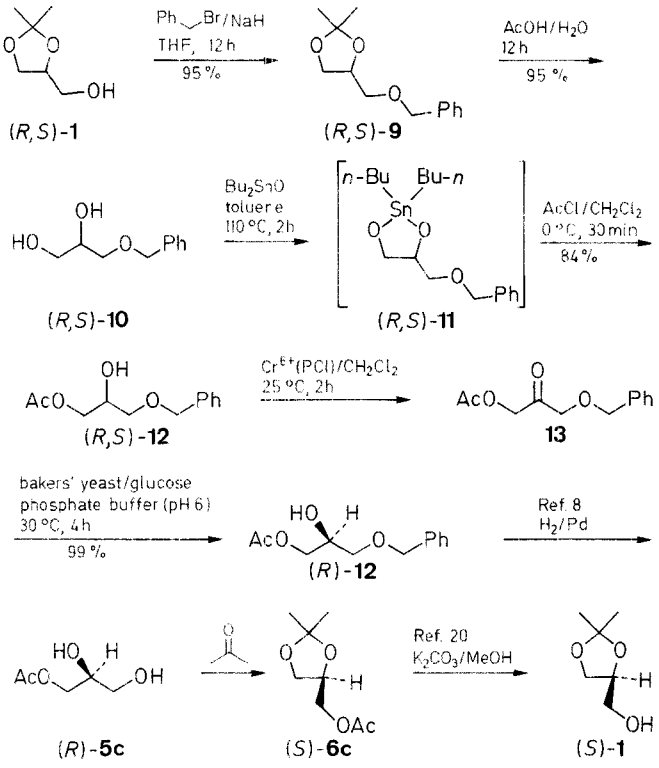


(*S*)-**5a,b** (*S*)-**7a,b** (*S*)-**8a,b**

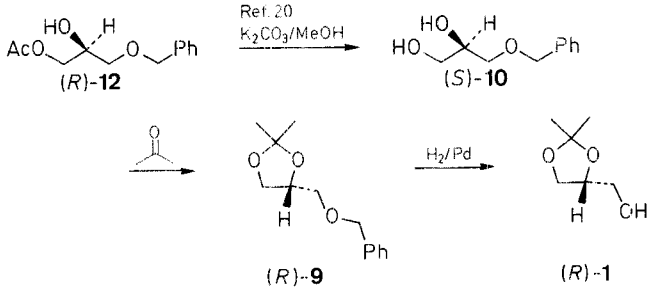
Oxiranylmethyl 4-nitrobenzoates have been shown to be at least as useful chiral building blocks as their parent epoxyalcohols.[14] They are reactive and versatile synthons. In particular, compound **8b** can be easily prepared by the catalytic modification of the asymmetric epoxidation of allyl alcohol using diisopropyl D-(−)-tartrate as chiral auxiliary reagent, followed by *in situ* derivatization.[15]

On the basis of the above-mentioned results, the bioreduction of 1-acetoxy-3-benzyloxypropanone **(13)** with fermenting yeast should give (*R*)-1-acetoxy-3-benzyloxy-2-propanol[(*R*)-**(12)**] and thus provide an opportunity for the facile preparation of (*S*)-**1** and (*R*)-**1**. The whole sequence then consists of the following steps: 1,2-*O*-isopropylideneglycerol [(*R,S*)-**1**] is *O*-benzylated with benzyl bromide and the *O*-benzyl derivative (*R,S*)-**9** is hydrolyzed with aqueous acetic acid to give (*R,S*)-3-benzyloxy-1,2-propanediol [(*R,S*)-**10**] which is converted into 4-benzyloxymethyl-2,2-dibutyl-1,3,2-dioxastannolane [(*R,S*)-**11**] by reaction with dibutyltin oxide in toluene; this cyclic acetal **11** of dibutyltin oxide is not isolated but is directly ring-cleaved by treatment with acetyl chloride in dichloromethane to give

(*R,S*)-1-acetoxy-3-benzyloxy-2-propanol [(*R,S*)-**12**] which is oxidized to 1-acetoxy-3-benzyloxypropanone (**13**) with pyridinium chlorochromate (PCC) in dichloromethane; reduction of ketone **13** with fermenting bakers' yeast then affords pure (*R*)-1-acetoxy-3-benzyloxy-2-propanol [(*R*)-**12**]; hydrogenolysis of (*R*)-**12** gives (*R*)-3-acetoxy-1,2-propanediol[8] [(*R*)-**5c**] which is converted into (*R*)-4-acetoxy-2,2-dimethyl-1,3-dioxolane [(*S*)-**6c**]; hydrolysis of the *O*-acetyl group in (*S*)-**6c** with potassium carbonate in aqueous methanol finally affords (*S*-1,2-*O*-isopropylideneglycerol[20]](*S*)-**1**].



The enantiomer (*R*)-**1** can be prepared by hydrolysis of (*R*)-**12** with potassium carbonate in methanol, conversion of the resultant (*S*)-1-benzyloxy-2,3-propanediol[20] [(*S*)-**10**] into its *O,O*-isopropylidene derivative (*R*)-**9** by reaction with acetone, and hydrogenolysis of the *O*-benzyl group in (*R*)-**9**.



Optical rotations were measured in a 1-dm cell of 1-mL capacity using a Perkin-Elmer 241 polarimeter. Microanalyses were performed with a Perkin-Elmer 240 instrument. Silica gel 60 F_{254} plates (Merck) were used for analytical TLC and 270–400 mesh silica gel (Merck) for flash chromatography. GLC analyses were performed on a Dani 3900 instrument with a capillary SE-52 column using a Hewlett-Packard 3390 integrator. ^{1}H-NMR spectra were recorded with a Bruker WP-80 instrument.

"Dry" solvents were distilled under dry N_2 immediately before use: CH_2Cl_2 was distilled from CaH_2 and pyridine was distilled from BaO. All reactions employing dry solvents were performed under N_2 (from liquid N_2).

1-Benzoyloxy-3-hydroxypropanone (4a):
Benzoyl chloride (280 mg, 2 mmol) is slowly added to a stirred solution of 1,3-dihydroxypropanone (200 mg, 2 mmol) and 4-dimethylaminopyridine (10 mg, 0.08 mmol) in pyridine (8 mL) at −5 °C and stirring is continued for 30 min at room temperature. The solvent is evaporated at reduced pressure and the residue is partitioned between H_2O (5 mL) and EtOAc (10 mL). The aqueous phase is evaporated, and unreacted 1,3-dihydroxypropanone is recovered (30%). The organic layer is washed with 5% $NaHCO_3$ solution (2 mL), dried (Na_2SO_4), filtered, and evaporated at reduced pressure. The residue is purified by precipitation (EtOH/H_2O, 1:1) of the by-product 1,3-dibenzoyloxypropanone to give **4a**; yield: 250 mg (64%); mp 95–97 °C;

$C_{10}H_{10}O_4$	calc.	C 61.85	H 5.15
(194.1)	found	61.80	5.20

IR ($CHCl_3$): ν = 3570–3420 (OH), 1736 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$/TMS): δ = 4.45 (s, 2H, CH_2OH); 5.00 (s, 2H, CH_2OCO); 6.50 (br s, 1H, OH, exchangeable with D_2O); 7.40 (m, 3 H_{arom}); 8.00 (m, 2 H_{arom}).

3-Hydroxy-1-(4-nitrobenzoyloxy)propanone (4b):
This product is obtained in the same manner as **4a** from 1,3-dihydroxypropanone (200 mg, 2 mmol) and 4-nitrobenzoyl chloride (371 mg, 2 mmol); yield: 240 mg (50%); mp 114 °C.

$C_{10}H_9NO_6$	calc.	C 50.20	H 3.76	N 5.85
(239.1)	found	50.29	3.80	5.79

^{1}H-NMR ($CDCl_3$/TMS): δ = 4.1–4.4 (m, 3H, CH_2OH, OH; exchangeable with D_2O); 4.32 (s, 2H); 5.1 (s, 2H, CH_2OCO); 8.15 (s, 4 H_{arom}).

Asymmetric Reduction of Ketones 4a, b and 13 with Fermenting Yeast:

General Procedure: Fresh bakers' yeast [1.2 g, wet weight of cells (120 g/L)] is suspended in 0.2 M Na phosphate buffer (pH 6, 10 mL) containing glucose [1 g (100 g/L)]. This suspension is incubated at 30 °C for 30 min whereupon a solution of the ketone (5 g/L) is added: **4a** (50 mg) in EtOH/DMSO (1:1, 0.5 mL); **4b** and **13** (50 mg) in EtOH (0.5 mL). The mixture is incubated at 30 °C under gentle shaking. GLC control of the transformation reveals quantitative reduction within 4 h. The mixture is then extracted with EtOAc (3 × 10 mL); the extract is washed with 5% $NaHCO_3$ solution (10 mL), dried (Na_2SO_4), and evaporated to give the desired alcohol in quantitative yield.

Medium-Scale Procedure for the Reduction of Ketone **4a**: Fresh bakers' yeast (48 g, wet weight of cells) is suspended in 0.2 M Na phosphate buffer (pH 6; 320 mL) containing glucose (32 g). The mixture is placed in a fermentation bottle equipped with a gas trap and an opening for adding substrate, under limited O_2 supply and mild magnetic stirring. After 30–40 min at 30 °C, when vigorous gas evolution begins, a solution of ketone **4a** [3.073 g, (9.6 g/L)] in EtOH/DMSO (1:1, 5 mL) is added and the mixture is incubated at 30 °C. After 8 h, another portion of glucose (16 g) is added. After a total incubation time of 24 h, the mixture is extracted with EtOAc (3 × 60 mL); the extract is washed with 5% $NaHCO_3$ solution (30 mL), dried (Na_2SO_4), and evaporated to give product (*S*)-**5a**; yield: 3.0 g (99%).

(S)-1-Benzoyloxy-2,3-propanediol [(*S*)-**5a**]; mp 60–61 °C (benzene); $[\alpha]_D^{20}$ + 15.2° (*c* = 2, pyridine) (Lit.[9] $[\alpha]_D^{20}$ − 13.3° (*c* = 1.3, pyridine); e.e. > 99%, as determined in the following manner: Samples of product (*S*)-**5a** and racemic **5a** are *O*-acylated with (*R*)-(+)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride[12] pyridine in CCl_4 (25 °C, 18 h) and the resultant esters are analyzed by GLC (SE 52, 250 °C).

$C_{10}H_{12}O_4$	calc.	C 61.22	H 6.12
(196.1)	found	61.24	6.10

^{1}H-NMR ($CDCl_3$/TMS): δ = 3.7 (dd, 2H, CH_2O); 4.1 (m, 1H, CH); 4.4 (d, 2H, CH_2); 7.4–8.0 (m, 5 H_{arom}).

The absolute configuration of the product **5a** obtained from the reduction of **4a** is determined by comparison with the product obtained by *O*-benzoylation of (*R*)-1,2,-*O*-isopropylideneglycerol with benzoyl chloride/pyridine (0 °C) and subsequent hydrolysis of the cyclic acetal moiety with AcOH/H_2O.

(S)-1-(4-Nitrobenzoyloxy-2,3-propanediol [(*S*)-**5b**]: mp 83–84 °C (benzene) (Lit.[17] mp 82–84 °C; $[\alpha]_D^{20}$ + 18.8° (*c* = 2, EtOH) (Lit.[17] $[\alpha]_D^{20}$ – 17.1° (*c* = 5, EtOH).

$C_{10}H_{11}NO_6$	calc.	C 49.79	H 4.59	N 5.81
(240.1)	found	49.79	4.58	5.80

H^1-NMR ($CDCl_3$/TMS): δ = 1.6 (br s, 1 H, OH exchangeable with D_2O); 2.2 (br s, 1 H, OH exchangeable with D_2O); 4.1 (m, 1 H, CH); 4.4 (m, 2 H, CH_2OCO); 8.2 (s, 4 H_{arom}).

(R)-3-Acetoxy-1-benzyloxy-2-propanol [(*R*)-**12**]; e.e. ≥ 99%, determined as for (*S*)-**5a**. The configuration of (*R*)-**12** is proven by comparison with (*R*)-**12** obtained from (*R*)-**1** by *O*-benzylation and acetal cleavage.

$C_{12}H_{16}O_4$	calc.	C 64.28	H 7.2
(224.2)	found	64.29	7.2

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.1 (s, 3 H, CH_3); 2.7 (br s, 1 H, OH exchangeable with D_2O); 3.5 (m, 2 H, CH_2O); 4.1 (s, 2 H, CH_2OAc); 3.9–4.2 (m, 1 H, CH); 4.5 (s, 2 H, CH_2Ar); 7.3 (s, 5 H_{arom}).

(*S*)-Benzoyloxymethyl)oxirane [(*S*)-8 a]:

(S)-1-Benzoyloxy-3-tosyloxy-2-propanol [(*S*)-**7a**]: A solution of tosyl chloride (260 mg, 1.37 mmol) in dry CH_2Cl_2 (5 mL) is added to a stirred solution of (*S*)-1-benzoyloxy-2,3-propanediol [(*S*)-**5a**; 270 mg, 1.37 mmol] in dry CH_2Cl_2 (5 mL)/pyridine (0.24 mL) at 0 °C and stirring is continued at room temperature for 12 h. The mixture is then brought to pH 5 with diluted aqueous HCl and extracted with CH_2Cl_2 (3 × 10 mL). The organic extract is dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The crude product (*S*)-**7a** is purified by flash chromatography (hexane/EtOAc, 6:4); yield: 335 mg (70%); mp 38–40 °C.

$C_{17}H_{18}O_6S$	calc.	C 58.26	H 5.17	
(350.5)	found	58.25	5.18	

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.40 (s, 3 H, $ArCH_3$); 3.65 (br s, 1 H, OH, exchangeable with D_2O); 3.95–4.55 (m, 5 H, 2 CH_2, CH); 7.10–8.20 (m, 9 H_{arom}).

(S)-Benzoyloxymethyl)oxirane [(*S*)-**8a**]: A solution of compound (*S*)-**7a** (335 mg, 0.95 mmol) in dry CH_2Cl_2 (5 mL) is added to a stirred suspension of NaH (29 mg, 0.95 mmol) in dry CH_2Cl_2 (2.5 mL) at 0 °C and stirring is continued at room temperature for 30 min. The mixture is then quenched with saturated NH_4Cl solution (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic phase is dried (Na_2SO_4), filtered, and evaporated at reduced pressure. The crude product (*S*)-**8a** is flash-chromatographed (hexane/EtOAc, 1:1); yield: 170 mg (99%). An analytical sample is obtained by distillation at low pressure; bp 170 °C/0.8 Torr; $[\alpha]_D^{20}$ + 27.5° (*c* = 2, pyridine).

$C_{10}H_{10}O_3$	calc.	C 67.41	H 5.61
(178.2)	found	67.45	5.74

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.7 (dd, *A*BX part, 1 H, *J* = 2.6, 4.8 Hz); 2.8 (dd, A*B*X part, 1 H, *J* = 4.1, 4.8 Hz), 3.3 (m, 1 H); 4.1 (dd, A*B*X part, 1 H, *J* = 6.0, 12.3 Hz); 4.6 (dd, *A*BX part, 1 H, *J* = 12.3, 3.3 Hz); 7.4 (m, 3 H_{arom}); 8.1 (m, 2 H_{arom}).

(*S*)-(4-Nitrobenzoyloxymethyl)oxirane [(*S*)-8b]:

This product is obtained from (*S*)-1-(4-nitrobenzoyloxy-2,3-propanediol [(*S*)-**5b**; 50 mg, 0.20 mmol] by a two-step procedure via (*S*)-**7b** analogous to that described for (*S*)-**8a**; yield of (*S*)-**8b**: 32 mg [70% from (*S*)-**5b**]; mp 59–60 °C (Et_2O); $[\alpha]_D^{20}$ + 37.7° (*c* = 0.9, $CHCl_3$) (Lit.[18] $[\alpha]_D^{20}$ + 37.9° (*c* = 3.38, $CHCl_3$)].

$C_{10}H_9NO_5$	calc.	C 53.83	H 4.06	N 6.27
(223.1)	found	53.84	4.06	6.28

IR (Nujol): ν = 3120, 2970, 2920, 2860, 1730, 1610, 1520, 1460 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.7 (dd *A*BX part, 1 H, *J* = 2.6, 4.8 Hz); 2.9 (dd, A*B*X part, 1 H, *J* = 4.2, 4.8 Hz); 3.3 (m, 1 H); 4.2 (dd, A*B*X part, 1 H, *J* = 6.45, 12 Hz, 4.7 (dd, *A*BX part, 1 H, *J* = 3.22, 12 Hz); 8.2 (s, 4 H_{arom}).

1-Acetoxy-3-benzyloxypropanone (13):

1-Acetoxy-3-benzyloxy-2-propanol [(*R,S*)-**12**]: A mixture of 1-benzyloxy-2,3-propanediol [(*R,S*)-**10**; 445 mg, 2.5 mmol], dibutyltin oxide (625 mg, 2.5 mmol), and 4 Å molecular sieves (2 g) in dry toluene (20 mL) is heated to reflux for 2 h. Toluene is then removed under reduced pressure and CH_2Cl_2 (16 mL) and dry THF (4 mL) are added. The mixture is then cooled to 0 °C, AcCl (0.10 mL, 1.5 mmol) is added dropwise and stirring is continued for 30 min. Then, Na phosphate buffer (pH 7.1; 10 mL) is added and the entire mixture is filtered through a celite pad and extracted with $CHCl_3$ (3 × 20 mL). The organic extract is dried (Na_2SO_4) and concentrated. The crude material is purified by flash chromatography (hexane/EtOAc, 1:1) to give product **12**; yield: 316 mg (84%); oil; bp 169–170 °C.

1-Acetoxy-3-benzyloxypropanone (**13**): Pyridinium chlorochromate (322 mg) is added to a stirred solution of compound **12** (225 mg, 1.00 mmol) in dry CH_2Cl_2 (10 mL) at room temperature. After 2 h, the mixture is diluted with Et_2O (10 mL) and filtered through a celite pad. The filtrate is evaporated under reduced pressure. The unreacted starting material **12** (50%) and the product **13** are isolated in pure form by flash chromatography (hexane/EtOAc, 1:1); yield of **13**: 110 mg (50%); oil.

$C_{12}H_{12}O_5$	calc.	C 61.03	H 5.12
(236.2)	found	61.01	5.13

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.15 (s, 3 H, C–CH_3); 4.13 (s, 2 H, CH_2OC); 4.6 (s, 2 H), CH_2OAc); 4.9 (s, 2 H, CH_2Ar); 7.32 (s, 5 H_{arom}).

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