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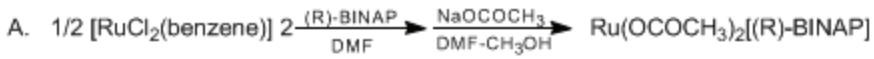
September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

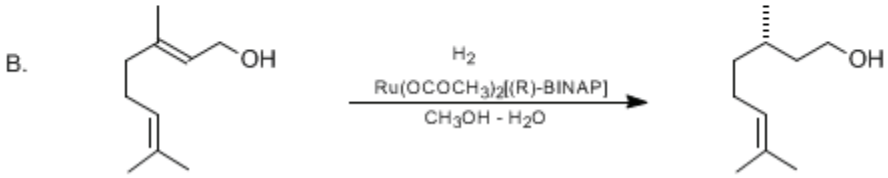
DOI:10.15227/orgsyn.072.0074

Organic Syntheses, Coll. Vol. 9, p.169 (1998); Vol. 72, p.74 (1995).

ASYMMETRIC HYDROGENATION OF ALLYLIC ALCOHOLS USING BINAP-RUTHENIUM COMPLEXES: (S)-(−)-CITRONELLOL

[6-Octen-1-ol, 3,7-dimethyl, (S)-]





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Checked by Andrew Madin and Larry E. Overman.

1. Procedure

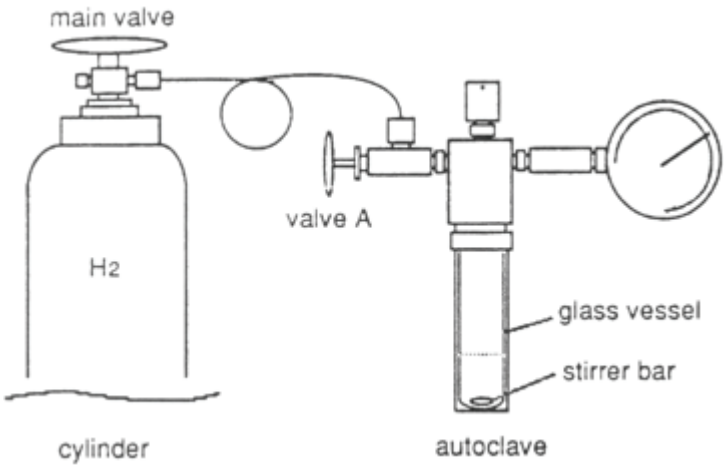
Caution! BINAP-Ru complexes are rapidly oxidized in solution in the presence of air, and all procedures should be carried out under anaerobic conditions using degassed solvents.

A. *[(R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium diacetate, $Ru(OCOCH_3)_2$[(R)-BINAP]*. A dry, 150-mL Schlenk tube (Note 1) connected to a supply of argon (Note 2) is equipped with a Teflon-coated magnetic stirring bar and a glass stopper. The vessel is charged with benzeneruthenium (II) chloride dimer, $[RuCl_2(benzene)]_2$ (800 mg, 1.60 mmol) (Note 3) and (R)-BINAP (1.89 g, 3.04 mmol) (Note 4), evacuated, and then filled with argon. N,N-Dimethylformamide (DMF) (30 mL) (Note 5) is introduced with a hypodermic syringe under the stream of argon. The reddish brown suspension is stirred at 100°C for 10 min (Note 6) and the resulting clear reddish brown solution (Note 7) is cooled. Another dry, 60-mL Schlenk tube is charged with sodium acetate (5.20 g, 63.4 mmol) and methanol (50 mL) (Note 8) and the solution is degassed by three freeze-thaw cycles. It is transferred into the DMF solution of BINAP-Ru(II) complex prepared above via cannula and the solution is stirred at 25°C for 5 min. To the solution are added water (50 mL) and toluene (25 mL) under argon and the resulting two layers are mixed by vigorous stirring. The upper organic layer is transferred into another 200-mL Schlenk tube (Note 9) using a cannula. The aqueous layer is vigorously mixed with toluene (25 mL) and the upper organic layer is again transferred into the Schlenk tube. This procedure is repeated once more. The combined organic layers are washed with four 10-mL portions of water (Note 10). Removal of the solvent at 1 mm and 40°C for 30 min with vigorous stirring (Note 11) and evacuation at 0.1 mm and 25°C for 12 hr gives 2.54–2.67 g of solid $Ru(OCOCH_3)_2$ [(R)-BINAP] (99–104% crude yield based on BINAP) (Note 12). It is dissolved in toluene (20–25 mL) with heating. Hexane (80–100 mL) is added very carefully to the solution down the side of the flask to form two layers. The solution is left at 25°C for 12 hr and then at 4°C for 3 days to give solid material. Removal of the mother liquor is followed by washing with hexane (20 mL) and drying under reduced pressure to afford 1.8–2.2 g (71–85% yield) of pure $Ru(OCOCH_3)_2$ [(R)-BINAP] as fine yellow needles or powdery crystals; mp 188–190°C dec (Note 13).

B. *(S)-(−)-Citronellol*. Geraniol (12.9 mL, 74 mmol) (Note 14) and 95% methanol (15 mL) (Note 15) are placed in a dry, 80-mL Schlenk tube and the mixture is degassed by five freeze-thaw cycles.

Another dry, 80-mL Schlenk tube, equipped with a rubber septum and a magnetic stirring bar and filled with argon, is charged with $Ru(OCOCH_3)_2$ [(R)-BINAP] (45 mg, 53 μmol) (Note 16). The system is evacuated and refilled with argon three times. By use of a cannula, the solution of geraniol in methanol is introduced into the Schlenk tube containing the ruthenium complex under argon. The resulting light yellow solution (Note 17) is then transferred with a cannula into a 100-mL, stainless steel autoclave equipped with a glass vessel (Note 18) and a magnetic stirring bar by use of a slight positive pressure of argon. The autoclave is connected to a hydrogen source (Note 19) using the arrangement shown in Figure 1, and the air originally present in the gas-inlet tube is replaced by hydrogen (Note 20). Valve A is opened and hydrogen is introduced until pressure gauge B indicates 100 atm. The solution is stirred at 20°C for 8–16 hr (Note 21). During hydrogenation, the hydrogen pressure is kept above 90 atm by the occasional introduction of hydrogen from the cylinder (Note 22). When consumption of hydrogen ceases, the gas-inlet tube is disconnected. Excess hydrogen is carefully released by opening valve A and then the apparatus is disassembled. The yellowish brown contents (Note 23) are transferred to a 50-mL flask and the solvent is removed by a rotary evaporator. The residue (Note 24) is distilled under reduced pressure to give 10.7–11.2 g (93–97% yield) of (S)-(−)-citronellol in 98% ee (Note 25) and (Note 26); bp 58–62°C/0.01 mm.

Figure 1



2. Notes

1. Before use, all apparatus is dried overnight in a 120°C oven.
2. Argon (99.998%) is purified by passing through a BASF catalyst RC-11 column at 80°C and then through 4 Å molecular sieves.
3. $[RuCl_2(benzene)]_2$, available from Aldrich Chemical Company, Inc., is used without purification.
4. BINAP [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] is commercially available or can be prepared according to a literature procedure.[3] The diphosphine is slowly oxidized in air to give the corresponding mono- and diphosphine oxides that can be removed by column chromatography (silica gel, benzene) under an inert atmosphere.
5. Guaranteed grade DMF, available from NACALAI TESQUE, Inc., is distilled over 4 Å molecular sieves under argon before use and stored in a 100-mL Schlenk tube. It is degassed by three freeze-thaw cycles.
6. Reaction at a higher temperature for a longer period leads to formation of the ruthenium carbonyl complex [IR(KBr) 1964 cm^{-1}].
7. The solution may be a crude mixture of cationic BINAP-Ru(II) complexes such as $[RuCl(BINAP)(DMF)_3]Cl$ and $[Ru(BINAP)(DMF)_4]Cl_2$. Physical properties include conductivity, 27 Scm^2/mol (DMF); ^{31}P NMR (4:1 DMF-$CDCl_3$) δ: 60.6 (d, J = 46), 61.4 (d, J = 46), 61.8 (s). The (R)-BINAP-Ru(II) complex obtained by removal of the solvent can catalyze hydrogenation of geraniol (98.7% pure commercial geraniol containing 1.3% of nerol, distilled from 4 Å molecular sieves). However, in addition to (S)-citronellol in 95–96% ee, dihydrocitronellol, an overreduction product, is obtained in 3–7% yield (1.1 M substrate in 95% aqueous methanol, 1.7 mM catalyst, 100 atm of H_2, 20°C, 8 hr).

8. Guaranteed grade methanol is distilled under argon.
9. The diameter is about 4 cm.
10. The extraction procedure must be carried out under an argon atmosphere.
11. Under reduced pressure, the solution sometimes foams. This can be avoided by heating the top part of the Schlenk tube with a hot air gun.
12. Crude BINAP-Ru complex with consistent spectral characteristics can be used for hydrogenation of geraniol (98.7% pure commercial geraniol containing 1.3% of nerol, distilled from 4 Å molecular sieves, 4.7 M substrate in 95% aqueous methanol, 2.8 mM $Ru(OCOCH_3)_2$ [(R)-BINAP], 100 atm of H_2, 20°C, 8 hr), to give (S)-citronellol in 96% ee, 97% isolated yield.
13. The product has the following spectral properties: ^{1}H NMR ($CDCl_3$) δ: 1.80 (s, 2 $OCOCH_3$), 6.47–7.84 (m, aromatic protons); ^{31}P NMR ($CDCl_3$) δ: 65.13 (s); ^{13}C NMR ($CDCl_3$) δ:23.50, 125.2–138.3, 188.1; IR (CH_2Cl_2) cm^{-1}: 1452, 1518. An analytical sample is prepared by drying at 110°C and 0.01 mm for 12 hr: Calcd for $C_{48}H_{38}O_4P_2Ru$: C, 68.5; H, 4.6. Found: C, 68.4; H, 4.5.
14. Pure geraniol is obtained by fractional distillation using a 1000 theoretical plate column. The checkers obtained geraniol, > 99.5% purity by GC analysis, from Fluka Chemical Company and used it directly.
15. The 95% methanol is prepared by mixing distilled, guaranteed methanol (95 mL) and water (5 mL). If absolute methanol or 90% aqueous methanol is used as solvent, somewhat longer reaction times are needed.
16. The complex can be stored under argon without noticeable loss of catalytic activity. It is weighed under an argon atmosphere.
17. The ruthenium complex is moderately soluble in methanol. Ultrasonic stirring is employed for complete solution.
18. A glass vessel is used for keeping the reaction mixture away from the stainless steel wall. The reaction system is evacuated and filled with argon three times before use.
19. The purity of hydrogen (Nippon Sanso Co.) used by the submitters is 99.99999%. The checkers used hydrogen of 99.99% purity.
20. The gas-inlet tube is attached to the autoclave and then the main valve of the cylinder is opened. After closing the main valve of the cylinder, the connector of the gas-inlet tube is loosened to release hydrogen pressure and tightened immediately. This procedure is repeated five times.
21. To maintain an internal temperature of 20°C the checkers placed the autoclave in a 18°C bath. Reactions terminated after 8 hr by the checkers showed the presence of unreacted geraniol (2–4%).
22. Enantioselectivity is very dependent on hydrogen pressure. Optical purities of citronellol products are 70% and 95% at 4 and 30 atm, respectively. Thus, hydrogen pressure greater than 90 atm is required for high optical yields.
23. In air, the color gradually changes to dark green.
24. Gas chromatographic analysis indicates that this consists of 97–99% of citronellol and 1–3% of dihydrocitronellol; column, SHIMADZU HiCap-CBP20, 25 m × 0.2-mm fused silica; column temperature, 140°C; injection temperature 160°C; helium pressure as carrier gas, 1.0 kg/cm^2; t_R of geraniol, citronellol, and dihydrocitronellol are 16.2, 13.7, and 8.6 min, respectively.
25. The product has the following spectral properties; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (d, J = 6.6, $CH_2CH(CH_3)CH_2$), 1.18 (m, $CH_2CHHCH(CH_3)CH_2$), 1.36 (m, $CH_2CHHCH(CH_3)CHH$), 1.57 (m, $CH_2CH(CH_3)CHH$), 1.59 (s, $(CH_3)_2C{=}CH$), 1.67 (s, $(CH_3)_2C{=}CH$), 1.71 (s, CH_2CH_2OH), 1.97 (m, $(CH_3)_2C{=}CHCH_2$), 3.66 (m, CH_2CH_2OH), 5.08 (t, J = 6.96, $(CH_3)_2C$-CH), $[\alpha]_D^{29}$ −4.5° to −4.7° (neat) [lit.[4] $[\alpha]_D^{20}$ −4.76° (neat)]. The submitters determined the enantiomeric excess by HPLC analysis of the diastereomeric amide prepared by condensation of citronellic acid (Note 27), obtained by the Jones oxidation of the alcohol, and (R)-1-(1-naphthyl)ethylamine (Note 28). HPLC analysis of this amide (column, TOYO SODA SILICA-60, 4.6 × 500 mm, a 3:7 ether-hexane mixture; flow rate 1 mL/min; detection 254 nm light) showed two peaks with t_R at 33.0 and 36.0 min in 1:99 ratio assignable to the R,R- and R,S-diastereomers, respectively.
26. With a commercially available 98.7:1.3 mixture of geraniol and nerol as substrate, (S)-citronellol in 96% ee is obtained. See also (Note 7).
27. In a 100-mL, round-bottomed flask equipped with a magnetic stirring bar are placed β-citronellol (1.63 g, 10.4 mmol) and acetone (25 mL). To this is slowly added Jones reagent [$Na_2Cr_2O_7$ (0.73 M in H_2O)/H_2SO_4 (concn = 1/4.2 v/v)] at 0–5°C until the orange color remains unchanged. To this mixture is added 2-propanol (5 mL) to decompose excess Jones reagent. After the orange color disappears,

insoluble material is filtered off and the solvent is removed under reduced pressure. The residue is dissolved in ether (10 mL) and the solution is washed with brine (10 mL). The water layer is extracted with ether and the combined organic layers are extracted with 1 N aqueous sodium hydroxide (50 mL) at 0°C. The alkaline aqueous layer is acidified and extracted with three, 20-mL portions of ether at 0°C. The combined ether layers are dried over anhydrous magnesium sulfate and the solvent is evaporated. To the residue is added a small amount of benzene; the benzene is then removed under reduced pressure to give 977 mg (55% yield) of citronellic acid.

28. In a 50-mL, round-bottomed flask, equipped with a rubber septum and a magnetic stirring bar and filled with argon, are placed citronellic acid (112 mg, 0.658 mmol) and a solution of (R)-1-(1-naphthyl) ethylamine (140 mg, 0.818 mmol) (Note 29) in dry DMF (4 mL) (Note 5). To this mixture in an ice bath are added a solution of diethyl cyanophosphonate (224 mg, 1.37 mmol) (Note 30) in dry DMF (2 mL) and then dry triethylamine (0.1 mL). The mixture is stirred and the reaction is followed by TLC. When the carboxylic acid has been consumed, which takes approximately 2 hr at room temperature, the reaction mixture is dissolved in a mixture of benzene (5 mL) and ethyl acetate (5 mL). The mixture is washed successively with cold 5% hydrochloric acid, ice-water, saturated sodium hydrogen carbonate solution, and brine, dried over anhydrous sodium sulfate, and finally concentrated under vacuum to give 207 mg (97% yield) of the amide.

29. (R)-(+)-1-(1-Naphthyl)ethylamine is purchased from Aldrich Chemical Company, Inc. The reagent is purified by recrystallization of its tartaric acid salt three times from 94% aqueous methanol followed by treatment with base and distillation of the free amine.

30. Commercial grade diethyl cyanophosphonate is distilled under argon before use.

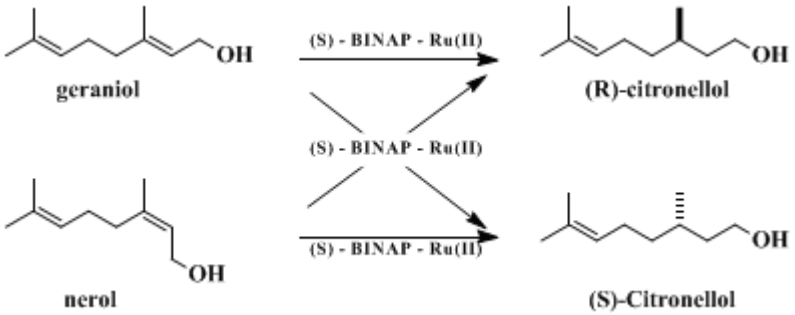
Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

The procedure for the synthesis of the title compound is a representative example of asymmetric hydrogenation in the presence of BINAP-Ru(II) diacetate.[5] The method is based on the synthesis of BINAP-Ru(II) dicarboxylate complexes[6] and enantioselective hydrogenation of geraniol.[7] The present method provides the first practical means for asymmetric synthesis of (S)- and (R)-citronellol. (S)-(−)-Citronellol of optical purity up to 92% can be obtained in a limited quantity from rose oil. A microbiological reduction of geraniol was reported to give enantiomerically pure (R)-(+)-citronellol.[8]

Nerol can also be used as a substrate. The stereochemical outcome is shown in Scheme 1, which indicates that the BINAP-Ru species differentiates the C(2) enantiofaces. The C(6)-C(7) double bonds are left intact. Thus, both R and S enantiomers are accessible by either variation of allylic olefin geometry or choice of handedness of the catalysts.



The complex formulated as $Ru(OCOCF_3)_2$ (BINAP), that is prepared from $Ru(OCOCH_3)_2$ (BINAP) and excess trifluoroacetic acid, shows high catalytic activity (S/C = 50000, 20°C, 100 atm, 96% ee). The cationic complex [RuI(BINAP)(p-cymene)]I[9] also acts as an efficient catalyst (96% ee). In the presence of the catalyst system derived from $Ru(OCOCH_3)_2$(BINAP) and 1 equiv of aqueous perchloric acid, hydrogenation proceeds very rapidly (S/C = 2000, completion after 15 min), but results in low

enantioselectivity (94% ee). ToIBINAP[10] [2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl] can also be used. Hydrogenation of geraniol using Ru_2Cl_4 $[(R)\text{-BINAP}]_2[N(C_2H_5)_3]$[11] as catalyst (6:1 ethanol-dichloromethane, H_2, 40 atm, 24°C, 90 hr) gives (S)-citronellol in 47% yield and 93% ee (92% conversion) in addition to dihydrocitronellol (40% yield) (see also (Note 7)).

This procedure has been successfully applied to the asymmetric synthesis of (3R,7R)-3,7,11-trimethyldodecanol, a versatile intermediate for synthesis of α-tocopherol (vitamin E). Hydrogenation of homogeraniol also proceeds smoothly to give 4,8-dimethylnon-7-enol in 92% ee in 96% yield. Hydrogenation of racemic allylic secondary alcohols in the presence of BINAP-Ru(II) diacetate brings about a high level of kinetic enantiomer selection.[12] This method provides a practical route to (R)-4-hydroxy-2-cyclopentenone, an important building block for the three-component prostaglandin synthesis.[13] A useful intermediate for synthesis of 1β-methylcarbapenems can be prepared by the hydrogenation of a chiral allylic alcohol.[14]

BINAP-ruthenium dicarboxylate complexes are also efficient catalysts for asymmetric hydrogenation of enamides, α,β– and β,γ-unsaturated carboxylic acids, α-amino ketones, and α-acylaminoacrylic acids.[5,15]

A detailed procedure for the asymmetric hydrogenation of β-ketoesters using a BINAP-ruthenium complex may be found on p. 589.[16]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 589

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

brine

Homogeraniol

(S)-(−)-CITRONELLOL

[(R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl]ruthenium diacetate, $Ru(OCOCH_3)_2$[(R)-BINAP]

benzeneruthenium(II) chloride dimer

BINAP-Ru(II) complex

$Ru(OCOCH_3)_2$ [(R)-BINAP]

ruthenium complex

BINAP [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl]

ruthenium carbonyl complex

BINAP-Ru(II) diacetate

(S)- and (R)-citronellol

$Ru(OCOCF_3)_2$ (BINAP)

$Ru(OCOCH_3)_2$ (BINAP)

$Ru(OCOCH_3)_2$(BINAP)

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ethyl acetate (141-78-6)

methanol (67-56-1)

ether (60-29-7)

sodium acetate (127-09-3)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium hydrogen carbonate (144-55-8)

allylic alcohol (107-18-6)

sodium sulfate (7757-82-6)

acetone (67-64-1)

toluene (108-88-3)

2-propanol (67-63-0)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

N,N-dimethylformamide,
DMF (68-12-2)

hexane (110-54-3)

geraniol (106-24-1)

triethylamine (121-44-8)

argon (7440-37-1)

perchloric acid (7601-90-3)

trifluoroacetic acid (76-05-1)

helium (7440-59-7)

nerol (106-25-2)

citronellol,
dihydrocitronellol,
β-citronellol (106-22-9)

(R)-4-hydroxy-2-cyclopentenone

(S)-Citronellol,
6-Octen-1-ol, 3,7-dimethyl, (S)- (7540-51-4)

citronellic acid (502-47-6)

(R)-1-(1-naphthyl)ethylamine,
(R)-(+)-1-(1-Naphthyl)ethylamine (42882-31-5)

diethyl cyanophosphonate (2942-58-7)

(R)-(+)-citronellol

(3R,7R)-3,7,11-trimethyldodecanol

4,8-dimethylnon-7-enol (163182-73-8)