

Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2007

Copper-Catalyzed Asymmetric Conjugate Addition of Trialkylaluminium Reagents to Trisubstituted Enones. Construction of Chiral Quaternary Centres.

M. Vuagnoux-d'Augustin, Prof. Dr. A. Alexakis*
Département de Chimie Organique
Université de Genève
30, quai Ernest Ansermet, CH-1211 Geneve (Switzerland)
Fax: (+) 41-22 379-32-15
E-mail: <u>Alexandre.Alexakis@chiorg.unige.ch</u>

Enantiomeric excesses were determined by chiral-GC (capillary column, 10 psi H_2), temperature programs are described as follows: initial temperature (°C) – initial time (min) – temperature gradient (°C/min) – final temperature (°C), or by chiral Supercritical Fluid Chromatography (SFC), with appropriated program using a gradient of methanol. Retention times (Rt) are given in minutes.

3-ethyl-3-methylcyclohexan-1-one 28: Enantiomeric excess was measured by chiral GC (lipodex E, isotherm 60°C, $Rt_1 = 32.8 \min (R)$, $Rt_2 = 43.3 \min (S)$).



3-*iso***butyl-3-methylcyclohexan-1-one 29:** Enantiomeric excess was measured by chiral GC (lipodex E, isotherm 80°C, $Rt_1 = 13.0 \min(S)$, $Rt_2 = 15.6 \min(R)$).



3-(but-3-enyl)-3-methylcyclohexan-1-one 31: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, $Rt_1 = 6.4 \min(S)$, $Rt_2 = 6.7 \min(R)$).



3-(pent-4-enyl)-3-methylcyclohexan-1-one 32: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130° C, Rt₁ = 10.1 min (*R*), Rt₂ = 10.5 min (*S*)).



3-(2-(1,3-dioxan-2-yl)ethyl)-3-methylcyclohexan-1-one 33: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, $Rt_1 = 36.7 \min(S)$, $Rt_2 = 37.4 \min(R)$).



3-(3-(1,3-dioxan-2-yl)propyl)-3-methylcyclohexan-1-one 34: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, 130-100-1-170-5, $Rt_1 = 141.1 \min(R)$, $Rt_2 = 141.8 \min(S)$).



3-methyl-3-phenylcyclohexan-1-one 35: Enantiomeric excess was measured by chiral GC (Hydrodex-B-3P, isotherm 140°C, $Rt_1 = 31.7 \min(R)$, $Rt_2 = 32.6 \min(S)$).



3-ethyl-3,5,5-trimethylcyclohexan-1-one 36: Enantiomeric excess was measured by chiral GC (chirasil DEX-CB, 60-110-2-170-5, $Rt_1 = 134.9 min(R)$, $Rt_2 = 135.5 min(S)$).



3-ethyl-3-methylcycloheptan-1-one 37: Enantiomeric excess was measured by chiral GC (Lipodex E, 60-0-1-170-5, $Rt_1 = 24.5 min (R)$, $Rt_2 = 25.7 min (S)$).



3-ethyl-3-methylcyclopentan-1-one 38: Enantiomeric excess was measured by chiral GC (lipodex E, isotherm 70°C, $Rt_1 = 9.1 \min(R)$, $Rt_2 = 10.2 \min(S)$).



Trans-2,3-dimethylcyclohexan-1-one 39: Enantiomeric excess was measured by chiral GC (Lipodex E, isotherm 70°C, *trans* adduct : $Rt_1 = 9.7 min (2S, 3R)$, $Rt_2 = 10.5 min (2R, 3S)$; *cis* adduct $Rt_1 = 12.5 min$, $Rt_2 = 13.2 min$).



3-ethyl-2-methylcyclohexan-1-one 40: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 70°C, $Rt_1 = 31.9 min (2S, 3R)$, $Rt_2 = 33.8 min (2R, 3S)$).



Trans-1-(2-methylcyclohexyl)ethan-2-one 41: Enantiomeric excess was measured by chiral GC (chirasil DEX CB, 60-0-1-115-20-170-5, *trans* adduct : $Rt_1 = 33.0 min (1S, 2S)$, $Rt_2 = 34.1 min (1R, 2R)$; *cis* adduct : $Rt_1 = 37.1 min (1S, 2R)$, $Rt_2 = 38.0 min (1R, 2S)$).



Trans-1-(2-ethylcyclohexyl)ethan-2-one 42: Enantiomeric excess was measured by chiral GC (chirasil DEX CB, 60-0-1-110-20-170-5, *trans* adduct: $Rt_1 = 41.6 min (1S, 2S)$, $Rt_2 = 42.3 min (1R, 2R)$; *cis* adduct: $Rt_1 = 43.8 min (1R, 2S)$, $Rt_2 = 44.8 min (1S, 2R)$).



(*R*)-7a-methyl-1,2,5,6,7,7a-hexahydroinden-4-one 43: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, $Rt_1 = 5.6 \min(S)$, $Rt_2 = 5.8 \min(R)$).



3-methyl-3-(4-(trifluoromethyl)phenyl)cyclohexan-1-one 44: Enantiomeric excess was measured by chiral SFC (AD-2%-2-1-15% MeOH, 200 Bars, 2 mL/min, 30°C, $Rt_1 = 3.8 min (R)$, $Rt_2 = 4.4 min (S)$).



3-(4-methoxyphenyl)-3-methylcyclohexan-1-one 45: Enantiomeric excess was measured by chiral SFC (OD H-2%-2-1-15% MeOH, 200 Bars, 2 mL/min, 30°C, $Rt_1 = 5.9 min (R)$, $Rt_2 = 6.4 min (S)$).



(*E*)-3-methyl-3-(pent-1-enyl)cyclohexan-1-one 49: Enantiomeric excess was measured by chiral GC (hydrodex B-6-TBDM, 60-0-1-170-5, $Rt_1 = 53.7 min (R)$, $Rt_2 = 55.4 min (S)$).



(*R*)-Allyl-3-ethyl-3-methylcyclohex-1-enyl carbonate 51: Enantiomeric excess was measured by chiral GC (Hydrodex-B6-TBDM, 60-0-1-170-5, $Rt_1 = 70.3$ (*R*), $Rt_2 = 50.1$ (*S*)).



(*S*)-4a-methyl-3,4,4a,5,6,7-hexahydronaphthalen-1(2H)-one 57: Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, 130-20-20-170-5, $Rt_1 = 17.6 min (R)$, $Rt_2 = 18.7 min (S)$).

