Supporting Information

Potassium Carbonate-Promoted Stereospecific 5-Endo-Trig Cyclization of Unactivated Allenes in the Absence of Any Transition Metals

Hiroaki Ohno, Yoichi Kadoh, Nobutaka Fujii, and Tetsuaki Tanaka

Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan, and Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

General Methods. Melting points are uncorrected. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ^1H NMR spectra were recorded in CDCl_3 . Chemical shifts are reported in parts per million downfield from internal Me_4Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, q = quartet, m = multiplet). Optical rotations were measured in CHCl_3 with a JASCO DIP-360 digital polarimeter. For flash chromatography, silica gel 60 H (silica gel for thin-layer chromatography, Merck) or silica gel 60 (finer than 230 mesh, Merck) was employed.

General Procedure for the Potassium Carbonate-Promoted Stereospecific 5-Endo-Trig Cyclization of Amino Allenes. Synthesis of (2S)-2-tert-Butyl-N-(2,4,6-trimethylphenylsulfonyl)-3-pyrroline (15). To a stirred suspension of K_2CO_3 (22.5 mg, 0.163 mmol) in DMF (2 mL) was added amino allene **11** (50.0 mg, 0.29 mmol), and the mixture was stirred for 20 h under reflux. Water was added to the mixture, and the whole was extracted with Et_2O . The extract was washed with water and brine, and dried over MgSO_4 . The filtrate was concentrated under reduced pressure to leave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane/EtOAc (20:1) to give 3-pyrroline **15** (39.2 mg, 78% yield): colorless oil; $[\alpha]_{\text{D}}^{25} +88.1$ (c 0.92, CHCl_3); IR (KBr) cm^{-1} : 1325 (SO_2N), 1153 (SO_2N); ^1H NMR (500 MHz, CDCl_3) δ 0.83 (s, 9H, CMe_3), 2.30 (s, 3H, CMe), 2.67 (s, 6H, $2 \times \text{CMe}$), 3.68–3.74 (m, 1H, 5- CHH), 4.23 (d, $J = 15.9$ Hz, 1H, 5- CHH), 4.54 (d, $J = 3.7$ Hz, 1H, 2-H), 5.85–5.89 (m, 2H, 3-H and 4-H), 6.95 (s, 2H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ 20.9, 23.1 (2C), 26.4 (3C), 36.8, 55.5, 75.9, 127.1, 129.3 (2C), 131.9 (2C), 133.0, 140.4, 142.5; MS (FAB) m/z (%) 308 (MH^+ , 100); HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{S}$ (MH^+) 308.1684; found 308.1710.

1H Line

Date : Wed Jun 29 11:22:06 2005

Filename : nmda
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non

POINT : 16384 points
 SAMPO : 16384 points
 FREQU : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 57.2 usec
 INTVL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3959 msec
 PREDL : 0.01000 msec
 ININT : 1000.0000 msec
 RESOL : 0.61 Hz
 PWT : 5.50 usec
 CNUC : 1H
 CNUC : 500.00 MHz
 OBSFQ : 162167.63 Hz
 RGAIN : 1.4

SCANS : 32 times

SLVNT : CDCl3
 SPINNT : 12 Hz
 TEMP : 22.2 C

1H Line

Date : Fri Jun 24 18:05:10 2005
 FileName : LoadingFID.mdata
 Comment : 1H Line
 SliceHistory :
 EXMODE : non
 POINT : 16384 points
 SAMPD : 16384 points
 FREQD : 10000.0 Hz
 FILTER : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 57.2 usec
 INTVL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INTWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 5.50 usec
 ORNUC : 1H
 ORFRO : 500.00 MHz
 ORSET : 162167.63 Hz
 RGAIN : 15
 SCANS : 32 times
 SOLVT : CDCl3
 SPINNT : 12 Hz
 TEMP : 22.8 C

1H Line

Date : Wed Jun 29 11:32:25 2005
 FileName : LoadingFID.mdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non
 POINT : 16384 points
 SAMPD : 16384 points
 FREQD : 100000.0 Hz
 F1L1R : 5000 Hz
 DELAY : 40.0 usec
 DEATD : 57.2 usec
 INVL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACOH : 1638.3999 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PM1 : 5.50 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162167.63 Hz
 RGAIN : 15
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNT : 13 Hz
 TEMP : 22.6 C

1H Line

Date : Mon Jun 20 20:26:30 2005

FileName : mmda
 Comment : 1H Line
 SliceHistory : non
 EXMODE :

POINT 16384 points
 SAMPD 16384 points
 FREQU 10000.0 Hz
 FILTR 5000 Hz
 DELAY 40.0 usec
 DEADT 57.2 usec
 INTVL 100.0 usec
 TIMES 32 times
 DUMMY 1 times
 PD 5.3616 sec
 ACQTM 1638.3999 msec
 PREDL 0.01000 msec
 ININT 1000.0000 msec
 RESOL 0.61 Hz
 PW1 5.50 usec
 OBNUC 1H
 OBPRO 500.00 MHz
 OBSET 162167.63 Hz
 RGAIN 14
 SCANS 32 times
 SLVNT CDCL3
 SPINNT 14 Hz
 TEM 22.2 C

1H Line

Date : Fri Jul 15 14:58:43 2005
 FileName : nmda
 Comment : 1H Line
 SliceHistory : non
 EXMODE : non
 POINT : 16384 points
 SAMPQ : 16384 points
 FREQ : 10000.0 Hz
 FIDTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 57.2 usec
 INVL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 5.50 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 182167.63 Hz
 RGAIN : 19
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNING : 13 Hz
 TEMP : 23.9 C

1H Line

Date : Fri Jul 8 11:27:05 2005
 FileName : LoadingID.nmdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :
 POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 57.2 usec
 INTVL : 100.0 usec
 TIMES : 32 times
 DUMMY : 1 times
 PD : 5.3616 sec
 ACQTM : 1638.3999 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 5.50 usec
 OBNUC : 1H
 OBPRQ : 500.00 MHz
 OBSET : 162167.63 Hz
 RGAIN : 16
 SCANS : 32 times
 SLVNT : CDCL3
 SPINNING : 16 Hz
 TEMP : 22.8 C

1H Line

Date : Fri Jul 22 14:25:21 2005
 FileName : LoadingFID.imdata
 Comment : 1H Line
 SliceHistory : non
 EXMODE :
 POINT : 16384 points
 SAMP0 : 16384 points
 FREQ0 : 10000.0 Hz
 F1FTR : 5000 Hz
 DELAY : 40.0 usec
 DEADT : 57.2 usec
 INIYL : 100.0 usec
 TIMES : 32 times
 DUMY : 1 times
 PD : 5.3616 sec
 ACQTH : 1638.3999 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.61 Hz
 PW1 : 5.50 usec
 1H : 500.00 MHz
 OBSF0 : 162167.63 Hz
 OBSF1 : 21
 RGAIN : 32 times
 SCANS :
 SLVNT : CDCL3
 SPINNT : 13 Hz
 TEMP : 24.1 C