Stereoselective Synthesis of α-(Dichloromethyl)amines, α-(Chloromethyl)amines, and α-Chloroaziridines

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General Procedures.

All commercial reagents and solvents were used directly as purchased without further purification. THF was distilled from sodium/benzophenone. N,N-Dimethylformamide was distilled from CaH₂. Flash chromatography was performed on silica gel with petroleum ether (PE)/EtOAc as the eluent. Melting points were uncorrected. Optical rotations were measured with a sodium lamp. ¹H NMR spectra were recorded at 400 MHz. Decoupled ¹³C NMR spectra were recorded at 100 MHz at the given temperatures. Chemical shifts (δ) are reported in parts per million and referenced to the residual solvent peak, and J values are given in hertz (Hz).
Determination of the configuration of compound 5c
Packing view of compound 5c

The Cl···O distance is 3.183Å
$^1$H NMR Spectra of the crude products 3

$^1$H NMR of crude product 3a

$^1$H NMR of crude product 3b
$^1$H NMR of crude product 3c

$^1$H NMR of crude product 3d
$^1$H NMR of crude product 3e

$^1$H NMR of crude product 3f
$^1$H NMR of crude product 3g

$^1$H NMR of crude product 3h
$^1$H NMR of crude product 3i

$^1$H NMR of crude product 3j
$^1$H NMR of crude product 3k
$^1$H NMR Spectra of the crude products 5

$^1$H NMR of crude product 5a

$^1$H NMR of crude product 5b
$^1$H NMR of crude product 5c

$^1$H NMR of crude product 5d
$^1$H NMR of crude product 5e

$^1$H NMR of crude product 5f
\(^1\)H NMR of crude product 3a via radical mono-dechlorination of compound 6a
LC-MS spectra of the crude products 3

3a, rt = 9.38 min; the other diastereomer, rt = 9.10 min
dr = 59.7 : 0.9 = 98 : 2

1a) HPLC spectroscopy

1b) Total ion current chromatogram

1c) Selected ion
3c, rt = 9.27 min; the other diastereomer, rt = 8.91 min

\[ \text{dr} = 98.8 : 1.11 = 98 : 2 \]

1a) HPLC spectroscopy

1b) Total ion current chromatogram

1c) Selected ion
3d, $rt = 6.00$ min; the other diastereomer, $rt = 5.67$ min

$dr = 9591 : 212 = 98 : 2$
3e, rt = 7.27 min; the other diastereomer, rt = 7.02 min

dr = 98.06 : 1.06 = 98 : 2

1a) HPLC spectroscopy

1b) Total ion current chromatogram

1c) Selected ion
3f, rt = 7.60 min; the other diastereomer, rt = 7.87 min

\[ \text{dr} = 61 : 59.8 = 98 : 2 \]
3g, rt = 8.07 min; the other diastereomer, rt = 7.19 min

dr = 5766 : 74 = 98 : 2
3h, $rt = 10.85$ min; the other diastereomer, $rt = 10.44$ min
$dr = 24.8 : 0.29 = 98 : 2$

1a) HPLC spectroscopy

1b) Total ion current chromatogram

1c) Selected ion
3i, rt = 8.59 min; the other diastereomer, rt = 8.07 min
dr = 28231 : 571 = 98 : 2
NMR Spectra for all new products

3a, $^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)
$^{1}H$ NMR (CDCl$_3$)
$3g, ^{13}C$ NMR (CDCl$_3$)
$\text{H} \cdot \text{N} \cdot \text{S} \cdot \text{O}$

$\text{C} \cdot \text{H} \cdot \text{Cl}_2$

$\text{H} \cdot \text{N}$

$\text{H} \cdot \text{N} \cdot \text{MR} \cdot (\text{CDCl}_3)$

$\text{f}$ (ppm)
3j, $^{13}$C NMR (CDCl$_3$)
3k, $^{13}$C NMR (CDCl$_3$)
3m. $^1$H NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)
3n, $^1$H NMR (CDCl$_3$)
51
$^{13}$C NMR (CDCl$_3$)

5a.
**5b, $^1$H NMR (CDCl$_3$)**

The NMR spectrum shows resonances corresponding to the chemical shifts provided.

- 9.0 ppm
- 8.5 ppm
- 8.0 ppm
- 7.5 ppm
- 7.0 ppm
- 6.5 ppm
- 6.0 ppm
- 5.5 ppm
- 5.0 ppm
- 4.5 ppm
- 4.0 ppm
- 3.5 ppm
- 3.0 ppm
- 2.5 ppm
- 2.0 ppm
- 1.5 ppm
- 1.0 ppm
- 0.5 ppm
$\text{5b, }^{13}\text{C NMR (CDCl}_3\text{)}$

![NMR spectrum image]

286 ppm

215.8

129.4

129.4

14.0

12.9

22.4
5d. $^1$H NMR (CDCl$_3$)
$5e, \textsuperscript{1}H$ NMR (CDCl$_3$)
5h. ^1^H NMR (CDCl$_3$)
7b. $^1$H NMR (CDCl$_3$)
$^{13}C$ NMR (CDCl$_3$)
7c. ^1H NMR (CDCl₃)
7c, $^{13}$C NMR (CDCl$_3$)
7e. $^{13}$C NMR (CDCl$_3$)
7f, $^{13}$C NMR (CDCl$_3$)