Supporting Information

Ring-Chain Tautomerism in Organic Synthesis: Synthesis of Heterocyclic Enamines from a Novel and Practical Formal Ring Transformation Reaction of Lactones

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1. Spectral data of compounds **3**

***tert*-Butyl 6-methanesulfonyloxy-3-oxohexanoate (3a).** Colorless oil: ^1H NMR (CDCl_3) δ 4.27 (t, $J = 6.1$, 2H), 3.38 (s, 2H), 3.01 (s, 3H), 2.73 (t, $J = 6.8$, 2H), 2.06 (quin, $J = 6.4$, 2H), 1.48 (s, 9H) (A trace amount of enol tautomer was observed from ^1H NMR spectra); ^{13}C NMR (CDCl_3) δ 201.9, 166.1, 81.9, 68.6, 50.2, 38.0, 37.0, 27.7, 22.7; IR (KBr) 1734, 1714, 1354, 1172 cm^{-1} ; MS (EI) m/z 207 (M-73, 3%), 165 (7), 57 (100).

***tert*-Butyl 6-methanesulfonyloxy-4-methoxy-3-oxohexanoate (3b).** Pale yellow oil: ^1H NMR (CDCl_3) δ 12.10 (s, 0.25H, OH), 5.12 (s, 0.25H, =CH), 4.35-4.20 (m, 2H), 3.85-3.78 (m, 0.75H), 3.69-3.62 (m, 0.25H), 3.45 (s, 1.5H), 3.39 (s, 2.25H), 3.33 (s, 0.75H), 2.98 (s, 3H), 2.19-2.05 (m, 2H), 1.46 (s, 2.25H), 1.42 (s, 6.75H); IR (KBr) 1738, 1718, 1356, 1174 cm^{-1} .

***tert*-Butyl 4-allyloxy-6-methanesulfonyloxy-3-oxohexanoate (3c).** Colorless oil: ^1H NMR (CDCl_3) δ 12.2 (s, 0.2H, OH), 5.98-5.82 (m, 1H), 5.34-5.19 (m, 1.8H, -CH=CH₂), 5.18 (s, 1H, =CH), 4.43-4.28 (m, 2H), 4.14-4.07 (m, 1H), 4.05-3.99 (m, 1.6H), 3.93-3.86 (m, 0.4H), 3.51 (s, 2H), 3.02 (s, 2.4H), 3.01 (s, 0.6H), 2.21-2.02 (m, 2H), 1.49 (s, 1.8H), 1.46 (s, 7.2H); IR (KBr) 1739, 1719, 1356, 1174 cm^{-1} .

***tert*-Butyl 4-benzyloxy-6-methanesulfonyloxy-3-oxohexanoate (3d).** Colorless oil: ^1H NMR (CDCl_3) δ 12.21 (s, 0.2H, OH), 7.34-7.25 (m, 5H), 5.21 (s, 0.2H, =CH), 4.90 (d, $J = 11.3$, 0.2H), 4.68 (d, $J = 11.3$, 0.2H), 4.60 (d, $J = 11.3$, 0.8H), 4.49 (d, $J = 11.3$, 0.8H), 4.40-4.20 (m, 2H), 4.08-4.03 (m, 0.8H), 3.98-3.93 (m, 0.2H), 3.48 (s, 1.6H), 2.90 (s, 2.4H), 2.86 (s, 0.6H), 2.20-2.00 (m, 2H), 1.48 (s, 1.8H), 1.41 (s, 7.2H). IR (KBr) 1738, 1719, 1356, 1175 cm^{-1} .

4.3.5. *tert*-Butyl 7-methanesulfonyloxy-3-oxoheptanoate (3e). Colorless liquid:
 ^1H NMR (CDCl_3) 4.24 (t, $J = 5.8$, 2H), 3.36 (s, 2H), 3.02 (s, 3H), 2.61 (t, $J = 6.7$, 2H), 1.76 (quin, $J = 6.4$, 2H), 1.47 (s, 9H) (A trace amount of enol tautomer was observed from ^1H NMR spectra); IR (KBr) 1739, 1713, 1353, 1174 cm^{-1} ; MS (EI) m/z 221 (M-73, 6%), 179 (22), 57 (100).

2. ^1H NMR spectra of 2 and 3, ^1H NMR and ^{13}C NMR spectra of 6a, 6d, 6g, 6j, 6m, 6o, 6s, 6x, 6y.

$$\begin{array}{c}
 \text{2a} \rightleftharpoons \text{2a'} \rightleftharpoons \text{2a''} \\
 \begin{array}{c}
 \text{HO} \quad \text{OC(CH}_3\text{)}_3 \\
 | \quad \quad | \\
 \text{C} \quad \quad \text{C} \\
 | \quad \quad | \\
 \text{CO}_2\text{C(CH}_3\text{)}_3 \quad \text{C=O} \\
 | \quad \quad | \\
 \text{C} \quad \quad \text{C} \\
 | \quad \quad | \\
 \text{HO} \quad \quad \text{OC(CH}_3\text{)}_3
 \end{array}
 \end{array}$$

¹H NMR of 2b

¹H NMR spectrum of compound **2b** (expansion)

The reaction scheme illustrates the equilibrium between three chemical species:

- 2c**: A cyclic acetal structure featuring a five-membered ring with an oxygen atom. A hydroxyl group (OH) and a 2-oxo-2-(trimethylsilyl)ethyl group (CO₂C(CH₃)₃) are attached to the ring. An OAlI group is attached to the carbon adjacent to the ring.
- 2c'**: An open-chain structure with a central carbon atom bonded to an OAlI group, a hydroxyl group (HO), and two trimethylsilylacetate groups (OC(CH₃)₃).
- 2c''**: An open-chain structure similar to 2c', but with a carboxylic acid group (COOH) instead of one of the trimethylsilylacetate groups.

Equilibrium arrows indicate the reversible nature of the transformations between 2c and 2c', and between 2c' and 2c''.

¹H NMR spectrum of 2c (expansion 1)

¹H NMR spectrum of compound **2c** (expansion 2)

¹H NMR of 3a

Current Data Parameters
 NAME zhangy
 EXPNO 6
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 981203
 Time 8.50
 INSTRUM dm3300
 PROBHD BBI

PULPROG zg
 TD 12046
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 3156.566 Hz
 FIDRES 0.262043 Hz
 AQ 1.9081364 sec
 RG 256
 DN 158.400 usec
 DE 4.50 usec
 TE 300.0 K
 D1 0.50000000 sec
 P1 3.00 usec
 SF01 300.1314286 MHz
 NUC1 1H
 PL1 0.00 dB

F2 - Processing parameters
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 WDW EM
 SSB 0
 LB -0.30 Hz
 GB 0.1
 PC 0.10

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 FIP 9.000 ppm
 F1 2401.04 Hz
 F2 -0.500 ppm
 F2 -150.07 Hz
 PPMCH 0.42500 ppm/cm
 HZCH 127.55525 Hz/cm

¹H NMR of 3b

¹H NMR spectrum of compound **3b** (expansion)

¹H NMR of 3c

¹H NMR spectrum of compound **3c** (expansion 1)

¹H NMR spectrum of compound 3c (expansion 2)

¹H NMR of 3d

¹H NMR of 6a

¹³C NMR of 6a

¹H NMR of 6d

¹³C NMR of 6d

¹H NMR of 6g

¹³C NMR of 6g

¹H NMR of 6j

¹³C NMR of 6j

¹H NMR of 6m

¹³C NMR of 6m

¹H NMR of 60

¹³C NMR of 60

¹H NMR of 6s

¹³C NMR of 6s

¹H NMR of **6x**

¹³C NMR of 6x

¹H NMR of 6y

¹³C NMR of 6y