An Annulation toward Fused Bicyclolactones

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Supporting information

All experiments were carried out under an air atmosphere. A.C.S. grade dichloromethane and distilled water were used without further purification. Column chromatography was performed over Sorbent silica gel 30-60 μ m. ^1H -NMR spectra were acquired by Varian 400 and 100MHz or 300 and 75MHz, respectively, and referenced to the internal solvent signals. IR spectra were recorded by ABB Bomem MB100 spectrometer. Mass spectra data and HRMS were obtained by Kratos MS25RFA Mass Spectrometer at McGill University.

Typical experimental procedure(entry 1, table 2):

To a screw-cap test tube capped with a septum, was added 1 mL of dichloromethane, ethyl benzoylacetate(47.3 μ L, 0.275 mmol), $\text{Ga}(\text{OTf})_3$ (19.5 mg, 0.0375 mmol), H_2O (9 μ L, 0.5 mmol) and HOTf(2 μ L, 0.0125 mmol). Then, 1,3-cyclooctadiene(31 μ L, 0.25 mmol) diluted in 1 mL of dichloromethane was added via a syringe pump over 8h at 40°C. The septum was then replaced by a screw-cap and the resulting solution was stirred at 60°C for 2 days. The excess of water was extracted with 2 portions of 5 mL of 5% NaHCO_3 . The combined organic layers were dried on MgSO_4 . The solvent was removed under reduced pressure and the product was isolated via column chromatography on silica gel(gradiant eluent: hexane: ethyl acetate = 60:1 to 2:1).

3-Cyclooct-2-enyl-1-pentane-2,4-dione. IR(neat): ν_{max} 2919, 1729, 1628, 1434, 1381, 1253, 1042, 919, 786 cm^{-1} ; ^1H NMR(CDCl_3 , 400MHz, ppm): δ = 5.77(dq, 1H, J =0.9, 5.7Hz), 5.09(td, 1H, J =0.9, 6.9 Hz), 3.65(d, 1H, J =6.3 Hz), 3.41(m, 1H), 2.28-2.06 (m, 8H), 1.72-1.42(m, 8H). ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 204.28, 204.13, 132.5, 129.7, 76.2,

36.9, 33.9, 31.3, 29.8, 28.4, 27.1, 25.6; MS(EI): $m/z(\%)$ 208(M^+), 165(100), 109, 43; HRMS calc'd for $C_{13}H_{20}O_2$: 208.1463; found, 208.1459.

3-Benzoyl-octahydro-cycloocta[b]furan-2-one. IR(neat): $\nu_{\max}$ = 2926,

1752, 1622, 1579, 1449, 1367, 1267, 1096, 777cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 8.02(m, 2H), 7.58-7.43(m, 3H), 4.54(td, 1H, J =3.3, 7.2Hz), 4.32(d, 1H, J =7.1Hz), 3.32(m, 1H), 2.27(m, 2H), 1.91-1.42(m, 10H); ^{13}C NMR(CDCl_3 , 100MHz, ppm): δ = 194.1, 171.7, 136.3, 134.2,

130.2, 129.6, 85.2, 57.7, 43.8, 34.9, 34.1, 28.1, 27.1, 25.0, 22.8; MS(EI): $m/z(\%)$ 272(M^+), 105(100), 77; HRMS: calc'd for $C_{17}H_{20}O_3$: 272.1412; found, 272.1415.

3-(4-Methyl-benzoyl)-octahydro-cycloocta[b]furan-2-one.

IR(neat): 2927, 2350, 1683, 1607, 1574, 1426, 1274, 982, 894cm^{-1} ;

^1H NMR(CDCl_3 , 300MHz, ppm): δ = 7.93(m, 2H), 7.31(m, 2H), 4.54(td, 1H, J =3.0, 6.9Hz), 4.30(d, 1H, J =7.2Hz), 3.21(m, 1H), 2.41(s, 3H), 2.33(m, 2H), 1.92-1.43(m, 10H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 195.9, 173.2, 130.5, 130.1, 129.6, 126.9, 85.2, 57.5, 43.9, 34.8, 34.1, 27.7, 27.1, 24.8, 22.2, 21.7; MS(EI): $m/z(\%)$ 286(M^+), 119(100); HRMS: calc'd for $C_{18}H_{22}O_3$: 286.1568; found, 286.1573.

3-(4-chloro-benzoyl)-octahydro-cycloocta[b]furan-2-one. IR(neat): 2853,

1745, 1689, 1588, 1446, 1269, 1013, 915cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 7.98(m, 2H), 7.49(m, 2H), 4.55(dt, 1H, J =3.6, 7.5Hz), 4.25(d, 1H, J =7.8Hz), 3.23(m, 1H), 2.28(m, 2H), 1.93-1.43(m, 10H); ^{13}C NMR(CDCl_3 ,

75MHz, ppm): δ = 191.6, 171.1, 140.8, 134.7, 131.1, 129.2, 85.3, 57.8, 43.4, 35.7, 34.3, 28.1, 27.1, 24.7, 22.3; MS(EI): $m/z(\%)$ 306(M^+), 167, 139(100); HRMS calc'd for $C_{17}H_{19}O_3^{35}\text{Cl}$: 306.1022; found, 306.1013. HRMS calc'd for $C_{17}H_{19}O_3^{37}\text{Cl}$: 308.0993; found, 308.0989.

3-Benzoyl-hexahydro-benzofuran-2-one. IR(neat): 2902, 1770,

1617, 1577, 1495, 1332, 1143, 1077, 860cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 8.07(m, 2H), 7.63-7.51(m, 3H), 4.84(m, 1H), 4.26(d, 1H, J =2.4Hz), 2.88(m, 1H), 2.08(m, 1H), 1.88(m, 1H), 1.80-1.68(m, 3H), 1.50-1.19(m, 3H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ =

195.8, 173.5, 135.5, 133.7, 129.5, 128.8, 78.7, 58.2, 39.3, 28.1, 27.2, 23.2, 20.2; MS(EI): m/z(%) 244(M⁺), 105(100), 77; HRMS calc'd for C₁₅H₁₆O₃: 244.1099; found, 244.1097.

3-(4-Methoxy-benzoyl)-octahydro-cycloocta[b]furan-2-one.

IR(neat): 2933, 1737, 1675, 1661, 1513, 1258, 1215, 1030, 995cm⁻¹;
¹H-NMR(CDCl₃, 300MHz, ppm): δ= 8.01(m, 2H), 6.98(m, 2H), 4.54(td, 1H, J=3.3, 7.1Hz), 4.27(d, 1H, J=8.4Hz), 3.89(s, 3H), 3.22(m, 1H), 2.27(m, 2H), 1.92(m, 10H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 195.8, 171.7, 132.1, 131.5, 131.2, 114.2, 85.2, 57.0, 55.9, 43.6, 34.4, 33.7, 27.7, 26.1, 24.1, 21.9; MS(EI): m/z(%) 302(M⁺), 194, 135(100); HRMS calc'd for C₁₈H₂₂O₄: 302.1518; found, 302.1521.

3-(4-Chloro-benzoyl)octahydro-cyclohepta[b]furan-2-one. IR(neat): 2926, 1746, 1683, 1583, 1489, 1301, 1296, 1033, 920cm⁻¹; ¹H NMR(CDCl₃, 300MHz, ppm): δ= 7.99(m, 2H), 7.49(m, 2H), 4.35(td, 1H, J=3.0, 7.5Hz), 4.26(d, 1H, J=9.0Hz), 3.10(m, 2H), 2.45(m, 2H), 1.93-1.48(m, 8H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 192.7, 171.5, 139.7, 135.0, 130.9, 129.2, 84.3, 56.9, 44.9, 33.1, 29.7, 27.7, 25.5, 25.1; MS(EI): m/z(%) 292(M⁺), 248, 139(100), 77; HRMS calc'd for C₁₆H₁₇O₃³⁵Cl: 292.0866; found, 292.0857. HRMS calc'd for C₁₆H₁₇O₃³⁷Cl: 294.0836; found, 294.0831.

3-(4-Bromobenzoyl)-octahydro-cycloocta[b]furan-2-one. IR(neat): 2925, 1742, 1687, 1585, 1486, 1381, 1292, 889cm⁻¹; ¹H NMR(CDCl₃, 300MHz, ppm): δ= 7.89(m, 2H), 7.65(m, 2H), 4.56 (td, 1H, J=3.6, 7.2Hz), 4.24 (d, 1H, J=7.1Hz), 3.22 (m, 1H), 2.27(m, 2H), 1.93-1.45 (m, 10H); ¹³C NMR(CDCl₃, 75MHz, ppm): δ= 191.8, 171.6, 135.1, 132.23, 131.1, 129.6, 85.3, 57.8, 43.4, 34.8, 34.1, 27.6, 27.0, 24.6, 22.3; MS(EI): m/z(%) 350(M⁺), 183(100), 84; HRMS calc'd for C₁₇H₁₉O₃⁷⁹Br: 350.0517; found, 350.0507. HRMS calc'd for C₁₇H₁₉O₃⁸¹Br: 352.0497; found, 352.0487.

3-(4-trifluoromethyl-benzoyl)octahydro-cycloocta[b]furan-2-one.

IR(neat): 2928, 1745, 1694, 1513, 1412, 1252, 1101, 923cm⁻¹; ¹H-NMR(CDCl₃, 300MHz, ppm): δ= 8.14(m, 2H), 7.78(m, 2H), 4.57(td, 1H, J=3.3, 7.8Hz), 4.30d, 1H, J=7.1Hz), 3.26(m, 1H), 2.28(m, 2H),

1.92-1.44(m, 10H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 191.4, 167.6, 138.1, 135.9(q, J =33Hz), 129.3, 125.9, 121.8 (q, J =270 Hz), 85.3, 55.3, 42.6, 34.8, 34.1, 29.9, 27.3, 27.0, 25.2; MS(EI) m/z (%): 340(M^+), 173(100), 145; HRMS calc'd for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{F}_3$: 340.1286; found: 340.1291.

3-(3-trifluoromethyl-benzoyl)octahydro-cycloocta[b]furan-2-one.

IR(neat): 2926, 1742, 1698, 1592, 1330, 1297, 1024, 952 cm^{-1} ; ^1H

NMR(CDCl_3 , 300MHz, ppm): δ = 8.27(m, 2H), 7.88(m, 1H), 7.65(m, 1H), 4.58(td, 1H, J =3.6, 7.4Hz), 4.30(d, 1H, J =7.8Hz), 2.25(m, 2H),

1.93-1.39 (m, 10H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 191.6, 167.9, 136.6, 132.8, 131.9(q, J =26Hz), 130.5, 129.5, 126.4, 121.9(q, J =270Hz), 85.4, 58.1, 43.4, 34.9, 34.1, 30.0, 27.7, 27.1, 24.9; MS(EI): m/z (%) 340(M^+), 173(100), 145; HRMS calc'd for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{F}_3$: 340.1286; found, 340.1280.

Ethyl 2-((Z)-cyclooct-2-enyl)-3-oxo-3-phenylpropanoate.

(From the mixture of diastereoisomers and some peaks are difficult to distinguished) IR(neat): 2846, 1671, 1588, 1425, 1388, 1260, 1125, 1031 cm^{-1} ; ^1H NMR(CDCl_3 , 300MHz, ppm): δ = 5.77(m, 1H), 5.37(m,

1H), 4.15(m, 2H), 2.36(m, 2H); ^{13}C NMR(CDCl_3 , 75MHz, ppm): δ = 199.6, 177.2, 133.7, 131.8, 130.7, 129.9, 128.9, 128.5, 61.6, 60.1, 36.9, 34.3, 33.7, 29.9, 27.1, 25.9, 14.5; MS(EI): m/z (%) 300(M^+), 192, 108, 105(100), 77; HRMS calc'd for $\text{C}_{19}\text{H}_{24}\text{O}_3$: 300.1725; found, 300.1728.

183

Data Collected On: m400-mercuri400
 Archive directory: /export/home/izhaac/vmr/sys/data
 Sample directory:
 File: PROTON

Pulse Sequence: zgpg30

Solvent: CDCl3

Temp: 23.0 C / 296.1 K

Relax. delay: 1.000 sec

Acq. time: 1.566 sec

Width: 9410.3 Hz

136 repetitions

Observed: 100.1245714 MHz

DATA PROCESSING

FT size 32768

Total time 23 min

136

Data Collected on: m300-mercury300
 Archive directory: /export/home/rgunn/vnmrsys/data
 Sample directory:
 File: CARBON

Pulse Sequence: szpul

Solvent: CDCl3

Temp: 25.0 C / 298.1 K

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.815 sec

Width 18867.9 Hz

SSB Reference

DECOUPLE H1 300.061029 MHz

Power 35 dB

continuously on

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 809 hr

193c

Intermediate C-alkylation only no lactone

Data Collected on: m400-mercury400
Sample directory: /export/home/12hwo/vnmrsws/data
File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3

Temp: 23.0 C / 296.1 K

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.998 sec

Wait time 4.000 sec

116 repetitions

OBSERVE H1, 400.1245804 MHz

DATA PROCESSING

File size 32798

Total time 23 min

mixture of diastereoisomers

136

Data Collected on: a300-mercury300
Archive directory: /export/home/rgunn/vmarsys/data
Sample directory:
File: CARBON

Pulse Sequence: szpul

Solvent: CCl₄

Temp.: 25.0 C / 298.1 K

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.000 sec

Width 18667.9 Hz

15232 repetitions

OBSERVE C13, 75.4500158 MHz

DECOUPLE H1, 300.0610299 MHz

continuous on

WALTZ-16 modulated

DATA PROCESSING

Gamma 1.0 Hz

FT 5120 131072

Total time 809 hr

mixture of diastereoisomers

135

Data Collected on: s300-mercury300
Archive directory: /export/home/rgunn/vmr/sys/data
Sample directory:
File: CARBON

Pulse Sequence: zgpg30

Solvent: CDCl3

Temp.: 25.3 C / 238.1 K

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.000 sec

Width 18667.5 Hz

15232 repetitions

OBSERVE C13, 75.450158 MHz

DECOUPLE H1, 308.0610235 MHz

Power 55 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT 520 131072

Total time 845 hr

136

Data Collected on: a300-mercury300
 Archive directory: /export/home/rgunn/vmarsys/data
 Sample directory:
 File: CARBON

Pulse Sequence: szpul
 Solvent: CCl₃
 Temp.: 25.0 C / 298.1 K
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.000 sec
 Width 18667.9 Hz
 15232 repetitions
 OBSERVE C13, 75.4500158 MHz
 DECOUPLE H1, 300.0610299 MHz
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Length of F2 1.0 Hz
 FT 5120 131072
 Total time 809 hr

13C OBSERVE

Data Collected on: m300-mercury300
Sample directory: /export/home/rgunn/vnmrsys/data
Sample name: 13C-1
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.815 sec

Width 18667.5 Hz

18000 repetitions

Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

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Observed on: 13C-1

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Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

Observed on: 13C-1

246H
 Data Collected on: m400-mercury400
 Archive directory: /export/home/lizhao/vnmrsws/data
 Sample directory: /export/home/lizhao/vnmrsws/data
 File: PROTON
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 Relax. delay 1.000 sec
 Aq. time 1.000 sec
 Acq. time 1.000 sec
 Width 6410.3 Hz
 48 repetitions
 OBSERVE F1, 400.1245662 MHz
 P1 12.000 sec
 P2 12.000 sec
 P1 size 32768
 Total time 23 min

Data Collected on: m300-mercury300
Archive directory: /export/home/rgunn/vnarsys/data
Sample directory:
File: CARBON

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Pulse Sequence: s2pul1
Solvent: CDCl3
Temp.: 55.0 C / 238.1 K
Relax. delay 1.000 sec
pulse 45.0 degrees
Acq. time 1.815 sec
Width 18867.9 Hz
FID file 188679.f
OBSERVE F2 13C 4500158 MHZ
DECOUPLE H1 300.0610299 MHZ
Power 35 dB
continuously on
WALTZ-16 modulated
Line frequency 125.760 MHz
Line broadening 1.0 Hz
FI size 131072
Total time 809 hr

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447

Data Collected on: m408-mercury400
 Sample directory: /export/home/lizhao/vnmrSYS/data
 File: PROTON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.998 sec
 Width 6410.3 Hz
 F2 400.1245662 MHz
 OBSERVED F1
 DATA PROCESSING
 FT size 32768
 Total time 3 min

850 248

Data Collected on: m400-mercury400
 Archive directory: /export/home/lzhao/vnmr/sys/data
 Sample directory: /export/home/lzhao/vnmr/sys/data
 File: rme248n

Pulse Sequence: szpul

Solvent: CDCl3
 Temp. 25.0 C / 298.1 K

Relax. delay 1.000 sec
 Pulse 45.0 degrees

Acq. time 1.398 sec
 Width 640.3 Hz

Observed on 400.1245662 MHz
 OBSERVE H1

DATA PROCESSING

FT size 32768
 Total time 46 min

136

Data Collected on: m300-mercury300
 Archive directory: /export/home/rgunn/vnmrSYS/data
 Sample directory:
 File: CARBON

Pulse Sequence: szpul

Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.815 sec
 VOLTAGE 1000 V
 15232 repetitions
 OBSERVE C13, 75.4500158 MHz
 DECOUPLE H1, 300.0610299 MHz
 Prescanned continuously on
 VOLTAGE 1000 V
 DATA PROCESSING
 F1 Processing 1.0 Hz
 F1 size 131072
 Total time 869 hr

t: C0013
25.0 C / 298.1 K
delay 1.000 sec
45.0 degrees
time 1.998 sec
6410.3 Hz
petitions
PROCESSING
E H1, 400.1245662 MHz
p 32768
time 23 min

Fc1ccc(cc1)C(=O)C23CCCCC2C3=O

12 10 8 6 4 2

136

Data Collected on: m300-mercury300
 Archive directory: /export/home/rgum/vnmrsys/data
 Sample directory:
 File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C / 298.1 K

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.815 sec

Width 18867.9 Hz

25.000 MHz

OBSERVE F13, 75.4500158 MHz

DECOUPLE H1, 300.0610299 MHz

Power 35 dB

Continuously on

Waltz16 decoupling

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 809 hr

Mechanistic experiment

A screw-cap NMR tube was charged with 0.5 mL of CD_2Cl_2 and ethyl benzoylacetate (8.7 μL , 0.05 mmol). A ^1H NMR was recorded (Figure S1). HOTf (8 μL , 0.05 mmol) and $\text{Ga}(\text{OTf})_3$ (26 mg, 0.0375 mmol) were added and the resulting mixture was shaken (some $\text{Ga}(\text{OTf})_3$ was still undissolved). Another ^1H NMR was recorded (Figure S2). Then, 1,3-cyclooctadiene (5.58 μL , 0.045 mmol) was added and the tube was heated to 60°C . The reaction was monitored by ^1H NMR. After 2h, intermediate **4** was observed (Figure S3). The NMR tube was then put into an oil bath at 60°C overnight and a final ^1H NMR was recorded (Figure S4).

Figure S1. Ethyl benzoylacetate alone in CD_2Cl_2

Figure S2. Ethyl benzoylacetate + HOTf(1 equiv.) + Ga(OTf)₃(1 equiv.)

Figure S3. Ethyl benzoylacetate + HOTf(1 equiv.) + Ga(OTf)₃(1 equiv.) + 1,3-cyclo-octadiene(0.9 equiv.) after 2h.

Figure S3. Ethyl benzoylacetate + HOTf(1 equiv.) + Ga(OTf)₃(1 equiv.) + 1,3-cyclo-octadiene(0.9 equiv.) after overnight.