Ruthenium-Catalyzed Oxidative Cleavage of Alkynes to Carboxylic Acids

Dan Yang,^{*,†,§} Fei Chen,[†] Ze-Min Dong,[†] and Dan-Wei Zhang[§]

[†]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China,

[§]Department of Chemistry, Fudan University, Shanghai 200433, China

yangdan@hku.hk

Supporting Information

Table of Contents:

The preparation and characterization data of compounds 10 and 12	S2
¹ H and ¹³ C NMR spectra of compounds 10 and 12	S3–S6

Preparation of 1-pent-3-ynyloxy-hexane (**10**)

To a stirred suspension of NaH (60 %, 0.78 g, 19.5 mmol) in dried THF (30 mL) at 0 °C under nitrogen was added 3-pentyn-1-ol (1.52 g, 18 mmol). After 30 min, 1-bromohexane (2.48 g, 15 mmol) and tetrabutylammonium bromide (0.167 g, 0.45 mmol) in THF (15 mL) were cannulated into the reaction mixture, and the reaction temperature was raised gradually to room temperature. After 1 h, the temperature was heated to reflux for 6 h. The reaction was quenched with saturated NH_4Cl solution, and the solvent was removed *in vacuo*. The residue was diluted with Et_2O , washed with water and brine successively, dried over anhydrous MgSO_4 , concentrated *in vacuo*, and purified by flash chromatography to afford **10** (1.55 g, 61%) as a colorless oil. ^1H NMR (CDCl_3 , 300 MHz): δ 3.50 (t, J = 7.2 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 2.40 (tq, J = 7.2, 2.6 Hz, 2H), 1.78 (t, J = 2.5 Hz, 3H), 1.59–1.55 (m, 2H), 1.34–1.25 (m, 6H), 0.89 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 76.2, 75.7, 70.9, 69.3, 31.5, 29.5, 25.7, 22.5, 19.0, 13.8, 3.2; IR (CH_2Cl_2) 1108 cm^{-1} ; EI-MS (20 eV) m/z 153 ($\text{M}^+ - \text{CH}_3$, 37), 97 (100), 85 (71); HRMS-EI m/z for $\text{C}_{10}\text{H}_{17}\text{O}$ ($\text{M}^+ - \text{CH}_3$) calcd 153.1279, found 153.1276.

Preparation of *tert*-butyl-pent-3-ynyloxy-diphenyl-silane (**12**)

3-Pentyn-1-ol (0.252 g, 3 mmol), *t*-butylchlorodiphenylsilane (0.907 g, 3.3 mmol), dried THF (10 mL) and imidazole (0.408 g, 6 mmol) were added sequentially into a 25 mL flask. After stirring for 9 h at room temperature under nitrogen, the reaction was quenched with saturated NH_4Cl solution, and diluted with Et_2O . The organic layer was washed with water and brine successively, dried over anhydrous MgSO_4 , concentrated *in vacuo*, and purified by flash chromatography to afford **12** (0.96 g, 99%) as a colorless oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.69–7.67 (m, 4H), 7.44–7.35 (m, 6H), 3.74 (t, J = 7.2 Hz, 2H), 2.40 (tq, J = 7.2, 2.6 Hz, 2H), 1.74 (t, J = 2.6, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.6, 133.8, 129.6, 127.6, 76.7, 76.1, 62.9, 26.8, 22.9, 19.1, 3.4; IR (CH_2Cl_2) 3079, 1616, 1478, 1111 cm^{-1} ; EI-MS (20 eV) m/z 266 ($\text{M}^+ - \text{C}_4\text{H}_8$, 22), 265 ($\text{M}^+ - \text{C}_4\text{H}_9$, 100); HRMS-EI m/z for $\text{C}_{17}\text{H}_{17}\text{OSi}$ ($\text{M}^+ - \text{C}_4\text{H}_9$) calcd 265.1049, found 265.1048.

Current Data Parameters
NAME fC-T1-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030503
Time 20.36
INSTRUM cp300
PROBHD QNP 5mm

PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2

SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 114
DM 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 9.00 usec
PL1 -6.00 dB
SF01 300.1315508 MHz

F2 - Processing parameters
SI 32768
SF 300.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 25.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 150.06500 Hz/cm

3.5222
3.4983
3.4746
3.4611
3.4388
3.4184
2.4303
2.4216
2.4136
2.4064
2.3979
2.3897
1.7871
1.7787
1.7701
1.5929
1.5793
1.5459
1.3411
1.3220
1.2962
1.2597
0.9070
0.8860
0.8626
0.0004
0.0018

7.2636

Integral

2.0089
1.9710
2.0008
3.0000
2.9093
6.7310
3.4640