SUPPLEMENTARY INFORMATION

Lithium Bromide as a Flexible, Mild, and Recyclable Catalyst for Solvent-Free Cannizzaro, Tishchenko, and Meerwein-Ponndorf-Verley Reactions

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1. Procedures

a) LiBr catalyzed Cannizzaro reactions

A mixture of LiBr (2 mmol), the aldehyde (4 mmol), and triethylamine (6 mmol) was stirred for 2 days at room temperature under inert atmosphere until complete consumption of the aldehyde was observed. Progress of the reaction was monitored by TLC and GC analyses. Then the mixture was stirred with excess H₂O for 2 hours and subsequently was extracted by ether. The volatile portion of the organic phase was evaporated after being dried over Na₂SO₄. Analysis of the residue by ¹H NMR and GC-MS showed the formation of the corresponding alcohol and carboxylic acid in equal amounts. The alcohol portion was separated by bulb to bulb distillation or by basic separation of the acid portion.

b) LiBr catalyzed Cannizzaro reactions to produce methyl ester

A mixture of LiBr (2 mmol), the aldehyde (4 mmol), and triethylamine (6 mmol) was stirred at room temperature under inert atmosphere for 2 days until complete consumption of the aldehyde was observed. Progress of the reaction was monitored by TLC and GC analyses. The mixture was stirred with excess methanol for 2h and diluted by ether. The organic phase was filtered and its volatile portion was evaporated under reduced pressure. Analysis of the residue by ¹H NMR and GC-MS showed the formation of the corresponding alcohol and methylester in equal amounts. The mixtures were fractionated by bulb to bulb distillation or by column chromatography over silicagel using hexane/EtOAc (ranging from 4:1 to 8:1).

c) LiBr catalyzed Tishchenko reactions

A mixture of LiBr (2 mmol), the aldehyde (4 mmol), and triethylamine (6 mmol) was stirred at room temperature under inert atmosphere for 2 days until complete consumption of the aldehyde was observed. Progress of the reaction was monitored by TLC and GC analyses. The mixture was diluted by ether, and the organic phase was evaporated after filtration. Analysis of the residue by ¹H NMR and GC-MS showed the formation of the corresponding ester. The mixtures were fractionated by bulb to bulb distillation or by column chromatography over silicagel using hexane/EtOAc (4:1).

d) LiBr catalyzed MPV reactions

A mixture of LiBr (10 mmol), aldehyde (10mmol), triethylamine (50 mmol) and isopropylalcohol (10 mmol) was stirred at room temperature under inert atmosphere for 2 days until complete consumption of the aldehyde was observed. Progress of the reaction was monitored by TLC and GC analyses. The mixture diluted by ether, and the organic phase was evaporated after filtration. Analysis of the residue by ¹H NMR and GC-MS showed the formation of the corresponding alcohol. The mixtures were fractionated by bulb to bulb distillation or by column chromatography over silicagel using hexane/EtOAc (4:1).

2. LiBr catalyzed MPV reactions of benzaldehyde using various secondary alcohols

3. Results obtained for the reactions using recycled catalyst

a) Cannizzaro reaction

No cycle	Yield%
0	97
1	92
2	90
3	87

b) Tishchenko Reaction

No cycle	Yield%
0	96
1	93
2	90
3	88

c) Meerwein-Ponndorf-Verley Reaction

No cycle	Yield%
0	98
1	93
2	91
3	90

table 1-entry3

-3.92937

7.84200
7.82653
7.72495
7.70632
7.44315
7.43185
7.42712
7.41593
7.41143
7.40010
7.27950
7.27585
7.26290
7.25924
7.24639
7.24266

3.004

1.012
1.000
1.162
1.125

Integral

Current Data Parameters
NAME Rahimi
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070316
Time 18.23
INSTRUM spect
PROBHD 5 mm GNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 80.6
DM 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 5.0000000 sec
MCREST 0.0000000 sec
MCWRK 0.0150000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters

SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 21.22 cm
F1P 10.405 ppm
F1 5203.60 Hz
F2P -0.124 ppm
F2 -61.87 Hz
PPMCM 0.52641 ppm/cm
HZCM 263.27390 Hz/cm

Current Data Parameters
 NAME Rehimi
 EXPNO 6
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070316
 Time 18.19
 INSTRUM spect
 PROBD 5 mm QNP 1H/13
 PULPROG zg30
 TO 65536
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1720407 sec
 RG 181
 DW 48.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 5.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 19.02 cm
 F1P 10.805 ppm
 F1 5403.98 Hz
 F2P -0.458 ppm
 F2 -228.86 Hz
 PPMCM 0.56314 ppm/cm
 HZCM 281.64185 Hz/cm

table 1-entry4

8.01904
 8.00180
 7.45731
 7.44009

Integral

3.0616

2.0824

2.0000

table 1-entry 5

Current Data Parameters
NAME Chem.Center
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070207
Time 14.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 128
DW 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 6.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 32.54 cm
F1P 12.319 ppm
F1 6160.96 Hz
F2P 0.366 ppm
F2 163.03 Hz
PPMCM 0.59764 ppm/cm
HZCM 298.89558 Hz/cm

ppm

8.16876
8.15295
7.63367
7.61905
7.60411
7.53266
7.51680
7.50024
7.48477
7.47546
7.46120
7.44602
7.42524
7.41105

table 2-entry 1

Current Data Parameters
NAME Zahedi
EXPNO 114
PROCNO 1

F2 - Acquisition Parameters

Date_ 20060717
Time 13.51
INSTRUM spect
PROBHD 5 mm BBI 1H-8B
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 28.5
DW 48.400 usec
DE 6.50 usec
TE 297.0 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters

SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 18.00 cm
CY 8.53 cm
F1P 10.592 ppm
F1 5297.35 Hz
F2P -0.008 ppm
F2 -3.87 Hz
PPMCM 0.58887 ppm/cm
HZCM 294.51215 Hz/cm

ppm

8.04410
8.02706
7.46544
7.44840
7.43146
7.41120
7.39369

table 2-entry 4

Integral

1.0251
1.0000
2.0086
1.0286

Current Data Parameters
NAME Zahedi
EXPNO 112
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060717
Time 12.04
INSTRUM spect
PROBHD 5 mm BBI 1H-88
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 128
DM 48.400 usec
DE 6.50 usec
TE 296.1 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 10.57 cm
F1P 11.130 ppm
F1 5566.45 Hz
F2P -0.384 ppm
F2 -192.15 Hz
PPMCM 0.63968 ppm/cm
HZCM 319.92218 Hz/cm

ppm

table 2-entry 5

Current Data Parameters
NAME Zahedi
EXPNO 110
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060717
Time 11.53
INSTRUM spect
PROBHD 5 mm BBI 1H-88
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 181
DW 48.400 usec
DE 6.50 usec
TE 296.0 K
D1 5.0000000 sec
MCREST 0.0000000 sec
MCWRK 0.0150000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 2.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 15.14 cm
F1P 11.293 ppm
F1 5647.88 Hz
F2P -0.245 ppm
F2 -122.35 Hz
PPMCM 0.64097 ppm/cm
HZCM 320.56851 Hz/cm

table 2-entry 6

Current Data Parameters
 NAME Chem-center
 EXPNO 31
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061128
 Time 10.27
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDC13
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.305176 Hz
 AQ 1.6385000 sec
 RG 322.5
 DW 50.000 usec
 DE 6.50 usec
 TE 298.0 K
 D1 5.0000000 sec
 MCREST 0.0000000 sec
 MCWRK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.30 usec
 PL1 2.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 18.59 cm
 F1P 12.192 ppm
 F1 6097.77 Hz
 F2P -0.073 ppm
 F2 -36.49 Hz
 PPMCM 0.66141 ppm/cm
 HZCM 340.79215 Hz/cm

table 2-entry 7

Current Data Parameters
NAME Dr.Sharifi
EXPNO 34
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061003
Time 13.26
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 90.5
DM 48.400 usec
DE 6.50 usec
TE 296.9 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1330000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 18.43 cm
F1P 12.462 ppm
F1 6232.60 Hz
F2P -0.336 ppm
F2 -167.87 Hz
PPMCM 0.71098 ppm/cm
HZCM 355.58151 Hz/cm

table 2-entry 8

Current Data Parameters
 NAME Dr.Sharifi
 EXPNO 32
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061003
 Time 13.03
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.315264 Hz
 AQ 1.5860696 sec
 RG 90.5
 DM 48.400 usec
 DE 6.50 usec
 TE 297.2 K
 D1 5.00000000 sec
 MCREST 0.00000000 sec
 MCWPK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 11.08 cm
 F1P 11.092 ppm
 F1 5547.63 Hz
 F2P -0.044 ppm
 F2 -21.90 Hz
 PPMCM 0.61868 ppm/cm
 HZCM 309.41830 Hz/cm

ppm

table 2-entry 9

Current Data Parameters
NAME Dr.Sharifi
EXPNO 36
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061003
Time 13.41
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 90.5
DW 48.400 usec
DE 6.50 usec
TE 296.8 K
D1 5.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 11.08 cm
F1P 11.339 ppm
F1 5671.15 Hz
F2P -0.403 ppm
F2 -201.56 Hz
PPMCM 0.65235 ppm/cm
HZCM 326.26163 Hz/cm

table 2-entry 10

Current Data Parameters
 NAME Dr.Sharifi
 EXPNO 28
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061003
 Time 12.44
 INSTRUM spect
 PROBHD 5 mm GNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.315264 Hz
 AQ 1.5860696 sec
 RG 161.3
 DW 48.400 usec
 DE 6.50 usec
 TE 297.5 K
 D1 5.0000000 sec
 MCREST 0.0000000 sec
 MCWK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 -3.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 18.00 cm
 CY 11.08 cm
 F1P 11.160 ppm
 F1 5581.32 Hz
 F2P -0.201 ppm
 F2 -100.50 Hz
 PPMCM 0.63115 ppm/cm
 HZCM 315.65659 Hz/cm

table 3-entry 2

7.30514
7.28872
7.27356
6.94947
6.93496
6.86514

4.62505

3.81129
3.62872

ppm

Current Data Parameters
NAME Akbarzadeh
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061226
Time 10:22
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 35.9
DM 48.400 usec
DE 6.50 usec
TE 291.2 K
D1 5.0000000 sec
MCREST 0.0000000 sec
MCPRK 0.0150000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 11.64 cm
F1P 10.001 ppm
F1 5001.58 Hz
F2P -0.232 ppm
F2 -115.89 Hz
P2MCM 0.56846 ppm/cm
HZCM 284.30347 Hz/cm

table 3-entry 4

0.13726

3.10622

4.65248

7.34013
7.33622
7.32443
7.32041
7.30855
7.12187
7.10646
7.08789
7.06861
7.00146
6.99658

Current Data Parameters
NAME Akbarzaden
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061226
Time 10.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 57
DW 48.400 usec
DE 6.50 usec
TE 291.3 K
D1 5.0000000 sec
MCREST 0.0000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 18.00 cm
CY 11.64 cm
F1P 11.363 ppm
F1 5683.11 Hz
F2P -0.280 ppm
F2 -139.80 Hz
P0MCM 0.64662 ppm/cm
HZCM 323.49481 Hz/cm

Current Data Parameters
NAME Sharifi-Ch.Cent
EXPNO 44
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070221
Time 11:53
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 128
DW 48.400 usec
DE 6.50 usec
TE 298.0 K
D1 5.0000000 sec
MCREST 0.0000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.50 usec
PL1 -3.00 dB
SF01 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 10.872 ppm
F1 5437.38 Hz
F2P 0.121 ppm
F2 60.58 Hz
PPMCM 0.53754 ppm/cm
HZCM 268.83990 Hz/cm

table 3-entry 8

table 3-entry 9

Current Data Parameters
 Name: Sharifi-Ch-Gent
 EXPNO: 43
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20070221
 Time: 11.44
 INSTRUM: spect
 PROBHD: 5 mm QNP 1H/13
 PULPROG: zg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 16
 DS: 2
 SWH: 10330.578 Hz
 FIDRES: 0.157632 Hz
 AQ: 3.1720407 sec
 RG: 143.7
 DM: 4B, 400 usec
 DE: 6.50 usec
 TE: 298.0 K
 D1: 5.00000000 sec
 MCREST: 0.00000000 sec
 MCWPK: 0.01500000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 10.50 usec
 PL1: -3.00 dB
 SF01: 500.1330885 MHz

F2 - Processing parameters
 SI: 32768
 SF: 500.1300000 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.00

1D NMR plot parameters
 CX: 20.00 cm
 CY: 8.59 cm
 F1P: 10.115 ppm
 F1: 5058.89 Hz
 F2P: -0.346 ppm
 F2: -173.20 Hz
 PPMCM: 0.52307 ppm/cm
 HZCM: 261.60406 Hz/cm