Bismuth Compounds in Organic Synthesis: Synthesis of Dioxanes, Dioxepines, and Dioxolanes Catalyzed by Bismuth(III) Triflate

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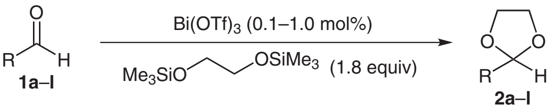
Abstract: A simple method for the synthesis of 1,3-dioxolanes from carbonyl compounds has been developed using 1,2-bis(trimethylsilyloxy)ethane in the presence of bismuth(III) triflate as a catalyst. The bismuth(III) triflate catalyzed synthesis of a range of dioxanes and dioxepines has also been developed. In these latter cases, the carbonyl compound is treated with a diol, and triethyl orthoformate is used as a water scavenger. All these methods avoid the use of a Dean–Stark trap.

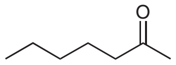
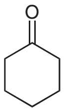
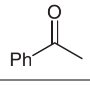
Key words: aldehydes, ketones, protection, cyclic acetals, 1,2-bis(trimethylsilyloxy)ethane

Aldehydes and ketones are frequently protected as cyclic acetals (dioxanes, dioxepines, and 1, 3-dioxolanes) in the course of a total synthesis.[1] In addition, acetals can be converted into a variety of other useful functional groups, and hence serve as useful intermediates in synthesis.[2] Thus, the conversion of a carbonyl compound into the corresponding cyclic acetal is an important synthetic transformation that has received much attention. The synthesis of cyclic acetals is usually carried out by reaction of the carbonyl compound with the corresponding diol in the presence of an acid catalyst.[3,4] Typically, this method requires the use of a toxic solvent such as benzene for azeotropic removal of water using a Dean–Stark trap. The use of a Dean–Stark trap is also not practical for very small-scale reactions. Several other methods that do not require protic acid catalysis have also been developed.[5] In addition, some mild methods for the formation of acetals under almost neutral[6] as well as basic conditions[7] have also been reported. Due to our continued interest in the use of bismuth compounds as environmentally friendly reagents[8] for organic synthesis, we undertook a study of the utility of bismuth triflate as a catalyst for cyclic acetal formation. Bismuth compounds have attracted considerable attention in the last decade due to their remarkably low toxicity, low cost, and good shelf life.[9,10] We have previously reported the use of bismuth triflate as a catalyst for the facile synthesis of acyclic acetals.[11] We now report a mild and efficient bismuth(III) triflate catalyzed synthesis of a range of cyclic acetals (Tables 1– 3).

Using commercially available 1,2-bis(trimethylsilyloxy)ethane, aldehydes and ketones were easily converted into the corresponding 1,3-dioxolane in good to excellent yields at room temperature. No additional solvent was necessary for the reaction, except for entry **1e** (Table 1).[12,13] It was possible to isolate the product by an

Table 1 Bismuth Triflate Catalyzed Conversion of Aldehydes and Ketones into 1,3-Dioxolanes



Entry	Substrate **1a–l** R	Bi(OTf)$_3$ (mol%)	Time[a]	Yield (%)[b,c] **2a–l**
a	2-ClC$_6$H$_4$	1.0	4 h	84[d,7a]
b	4-ClC$_6$H$_4$	0.1	1 h 40 min	95[7a]
c	2-BrC$_6$H$_4$	0.1	1 h 30 min	93[7a]
d	3-BrC$_6$H$_4$	0.1	1 h 15 min	97[14]
e	4-NO$_2$C$_6$H$_4$	0.1	1 h 20 min	91[e,15]
f	4-MeC$_6$H$_4$	0.1	2 h 10 min	86[d,7a]
g	4-MeOC$_6$H$_4$	1.0	41 h	85[f,16]
h	2,4-Cl$_2$C$_6$H$_3$	1.0	2 h 5 min	88[17]
i	Me(CH$_2$)$_8$	0.1	14 h	94[18]
j		1.0	2 h	85[d,18]
k		1.0	1 h 35 min	84[d,18]
l		1.0	6 h 30 min	89[19]

[a] Reaction progress was followed by GC or TLC.
[b] Refers to yield of pure, isolated product. All products were >98% pure, unless otherwise mentioned.
[c] Superscript against product refers to literature reference for product. Spectral data, when not reported previously, are provided in the experimental. New compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, and HRMS.
[d] Product was isolated by direct filtration of the reaction mixture through a silica gel column.
[e] Reaction was carried out in toluene at 100 °C (oil bath).
[f] Crude product was 94% pure by GC and ^{1}H NMR analysis. Remainder of the material was starting material.

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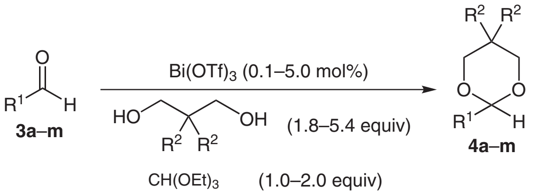
aqueous workup as well as by direct filtration of the reaction mixture through a silica gel column. The latter work up is especially desirable since it eliminates an aqueous waste stream. The procedure worked less well with an aldehyde containing strongly electron-donating group. For example, the conversion of *p*-anisaldehyde (entry **g**) into the corresponding dioxolane was very slow although high conversions were achieved.

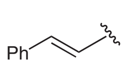
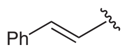
Since 1,3-bis(trimethylsilyloxy)propane, necessary for dioxane synthesis, is not readily commercially available, it was synthesized in lab.[20] The results of the attempted synthesis of dioxanes using 1,3-bis(trimethylsilyloxy)propane were not as promising as with dioxolane synthesis – higher catalyst loading (5–10 mol%), and longer reaction times (overnight) were needed to achieve the same degree of conversion as with dioxolanes. Hence, the dioxanes were synthesized by reacting the carbonyl compound with propane-1,3-diol in the presence of triethyl orthoformate, which serves as a water scavenger (Table 2). In only two cases (Table 2, entries **c** and **e**) was the formation of significant amounts of the corresponding diethyl acetal seen. Analysis of the crude product by ^{1}H NMR spectroscopy revealed the formation of the diethyl acetal to the extent of ca. 8% (entry **c**) and 20% (entry **e**), respectively. The diethyl acetal product had an R_f close to the dioxane, and hence it was difficult to completely separate the two, accounting for the moderate yield of the purified dioxane. Dioxanes could also be synthesized using 2,2-dimethylpropane-1,3-diol thereby illustrating the versatility of the method (Table 2, entries **i**–**m**). The diethyl acetal product was not observed when using 2,2-dimethylpropane-1,3-diol even though triethyl orthoformate was still used as a water scavenger.

Analysis of the crude dioxane product revealed that a small amount of the formate ester **5**, resulting from reaction of propane-1,3-diol with formic acid (generated by reaction of triethyl orthoformate with water) formed in all cases. In order to easily remove this product, the workup was modified to incorporate treatment of the reaction mixture with aqueous 2 M NaOH to hydrolyze the formate ester product into water-soluble products (Scheme 1).

The synthesis of dioxepines was also feasible, as shown in Table 3. In these cases, the yields were lower than those

Table 2 Bismuth Triflate Catalyzed Conversion of Aldehydes and Ketones into Dioxanes



Entry	**3a**–**m** R^1	R^2	Bi(OTf)$_3$ (mol%)	Diol (equiv)	CH(OEt)$_3$ (equiv)	Time[a]	Yield (%)[b,c] **4a**–**m**
a	4-MeC$_6$H$_4$	H	0.1	3.6	1.0	0 h 45 min	93[21]
b	4-ClC$_6$H$_4$	H	1.0	1.8	1.0	1 h 30 min	99[4g]
c	2-BrC$_6$H$_4$	H	1.0	1.8	1.0	2 h 35 min	78[22]
d	3-MeOC$_6$H$_4$	H	1.0	1.8	1.0	2 h	81[23]
e	4-OHC$_6$H$_4$	H	1.0	3.6	2.0	1 h 20 min	72[24]
f	4-TBSOC$_6$H$_4$	H	1.0	3.6	2.0	2 h 25 min	83[24]
g	Me(CH$_2$)$_8$	H	5.0	1.8	1.0	1 h 15 min	95[25]
h	 Ph	H	1.0	5.4	1.0	6 h	71[d,e,26]
i	4-MeOC$_6$H$_4$	Me	0.1	1.8	1.0	0 h 30 min	82[27]
j	4-MeC$_6$H$_4$	Me	0.1	1.8	1.0	1 h 30 min	96[27]
k	3-BrC$_6$H$_4$	Me	1.0	1.8	1.0	1 h 30 min	80[28]
l	4-ClC$_6$H$_4$	Me	1.0	1.8	0.3	4 h	83[27]
m	 Ph	Me	0.1	3.6	1.0	0 h 55 min	99[29]

[a] Reaction progress was followed by GC or TLC.

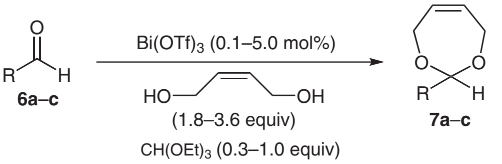
[b] Refers to yield of pure, isolated product. All products were >98% pure, unless otherwise mentioned.

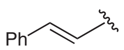
[c] Superscript against product refers to literature reference for product. Spectral data, when not previously reported, are provided in the experimental. New compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS.

[d] The product was 96% pure (remaining material was SM).

[e] Reaction was carried out in the presence of 0.50 g of anhyd MgSO$_4$.

Table 3 Bismuth Triflate Catalyzed Conversion of Aldehydes into Dioxepines

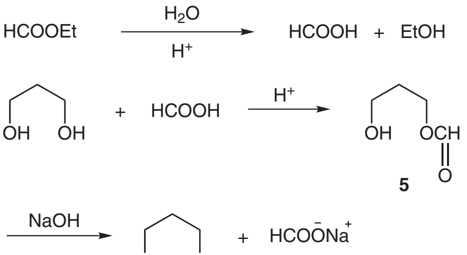


Entry	6a–c R	$Bi(OTf)_3$ (mol%)	Diol (equiv)	$CH(OEt)_3$ (equiv)	Time[a]	Yield (%)[b] 7a–c
a	$2-BrC_6H_4$	1.0	3.6	0.3	1 h 35 min	56[c]
b		0.1	1.8	1.0	4 h 15 min	60[30]
c	$Me(CH_2)_8$	5.0	3.6	0.3	1 h 45 min	86

[a] Reaction progress was followed by GC or TLC.

[b] Refers to yield of pure, isolated product. All products were >98% pure, unless otherwise mentioned. Superscript against product refers to literature reference for product. Spectral data, when not previously reported, are provided in the experimental. New compounds were characterized by ^1H and ^{13}C NMR spectroscopy and HRMS.

[c] Product was found to be 97% pure (remainder was starting material) by GC analysis and ^1H NMR spectroscopy.



Scheme 1

obtained with dioxolanes and dioxanes. Analysis of the crude reaction product showed formation of some unidentifiable side-products. In the case of entries **a** and **b** (Table 3), the crude product also contained ca. 12% unreacted aldehyde.

In summary, a mild and efficient bismuth(III) triflate catalyzed synthesis of a variety of dioxanes, dioxepines and dioxolanes has been developed. The use of a relatively nontoxic and easy to handle catalyst that avoids the use of a Dean–Stark trap makes this method especially attractive.

$Bi(OTf)_3$ was purchased from Aldrich Chemical Company and stored under vacuum. All other chemicals were purchased from Aldrich Chemical Company or Acros Organics. Products were analyzed using a JEOL Eclipse NMR spectrometer at 270 MHz for ^1H NMR and 67.5 MHz for ^{13}C NMR in $CDCl_3$ as the solvent unless otherwise mentioned. The progress of the reaction was followed by TLC or GC. GC analysis was performed on a Varian CP-3800 gas chromatograph equipped with a 30 m silica-packed column with a diameter of 0.25 mm (conditions: hold at 100 °C for 1 min; ramp at 30 °C/min until 220 °C; hold at 220 °C; flow rate; 2.0 mL/min of He). Thin-layer chromatography was performed on silica gel plates. Spots were visualized under UV light and/or by spraying the plate with phosphomolybdic acid followed by heating. Purifications were performed by flash chromatography on silica gel. Products were characterized by ^1H NMR, ^{13}C NMR, and GC analysis.

2-(3-Bromophenyl)-1,3-dioxolane (2d); Typical Procedure

Aqueous Workup: A mixture of 3-bromobenzaldehyde (**1d**; 1.00 g, 5.41 mmol) and 1,2-bis(trimethylsilyloxy)ethane (2.01 g, 2.39 mL, 9.73 mmol, 1.8 equiv) was stirred at r.t. as $Bi(OTf)_3·xH_2O$ (3.55 mg, 0.0054 mmol, 0.1 mol%) was added. The reaction progress was followed by GC. At 1 h 15 min, the reaction mixture was taken up in EtOAc (30 mL), washed with sat. aq $NaHCO_3$ (15 mL), brine (15 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to yield 1.58 g of a clear liquid. The crude product was purified by flash chromatography on silica gel (50 g, EtOAc–heptane, 20:80). Following a 50 mL prefraction, 24 (8 mL) fractions were collected, and fractions 13–20 were combined and concentrated to yield 1.20 g (97%) of **2d** as a clear liquid that was determined to be >99% pure by GC and ^1H NMR analysis. Owing to the small amount of catalyst used, no attempts were made to recover the catalyst from the aqueous layer. Note, however, that bismuth triflate has been recovered from organic solvents.[31]

^1H NMR ($CDCl_3$): δ = 3.92–4.18 (m, 4 H), 5.73 (s, 1 H), 7.29–7.64 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 66.5, 103.7, 123.2, 127.0, 130.8, 131.6, 133.2, 142.8.

2-(2-Chlorophenyl)-1,3-dioxolane (2a); Typical Procedure

Direct Filtration: A mixture of 2-chlorobenzaldehyde (**1a**; 0.500 g, 3.56 mmol) and 1,2-bis(trimethylsilyloxy)ethane (1.32 g, 1.57 mL, 6.40 mmol, 1.8 equiv) was stirred at r.t. as $Bi(OTf)_3·xH_2O$ (23.3 mg, 0.036 mmol, 1.0 mol%) was added. The reaction progress was followed by GC. At 4 h, the reaction mixture was loaded onto silica gel (61 g, EtOAc–heptane, 5:95, 15:85). A total of 41 (8 mL) fractions were collected, and fractions 31–40 were combined and concentrated to yield 0.55 g (84%) of **2a** that was determined to be >99% pure by GC and ^1H NMR analysis.

Spectral data not previously reported in the literature are given below.

2h

^1H NMR ($CDCl_3$): δ = 4.00–4.16 (m, 4 H), 6.07 (s, 1 H), 7.23–7.54 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 65.4, 100.2, 127.1, 128.6, 129.5, 133.8, 134.2, 135.4.

2i

^{1}H NMR (CDCl$_3$): δ = 0.80–0.85 (t, *J* = 6.6 Hz, 3 H), 1.22–1.39 (m, 14 H), 1.57–1.64 (m, 2 H), 3.76–3.94 (m, 4 H), 4.77–4.81 (t, *J* = 4.8 Hz, 1 H).

^{13}C NMR (CDCl$_3$): δ = 14.0, 22.6, 24.0, 29.3, 29.4, 29.5, 31.8, 33.9, 64.7, 104.6.

2j

^{1}H NMR (acetone-d_6): δ = 0.85–0.90 (t, *J* = 6.8 Hz, 3 H), 1.19–1.59 (m, 11 H), 3.83–3.89 (m, 4 H).

^{13}C NMR (acetone-d_6): δ = 13.9, 22.5, 23.6, 23.7, 32.0, 39.1, 64.5, 110.0.

2-(3-Methoxyphenyl)-1,3-dioxane (4d); Typical Procedure

A homogeneous mixture of 3-methoxybenzaldehyde (**3d**; 1.00 g, 7.34 mmol), propane-1,3-diol (1.01 g, 0.955 mL, 13.2 mmol, 1.8 equiv), and triethyl orthoformate (1.09 g, 1.22 mL, 7.34 mmol, 1.0 equiv) was stirred at r.t. as Bi(OTf)$_3$·xH$_2$O (48.2 mg, 0.0735 mmol, 1.0 mol%) was added. The reaction progress was followed by GC. At 2 h, aq 2 M NaOH (5 mL) was added to the reaction mixture, and then the mixture was stirred for 10 min. The mixture was extracted with Et$_2$O (2 × 20 mL). The combined organic layers were washed with H$_2$O (2 × 20 mL) and brine (15 mL), dried (MgSO$_4$), and concentrated on a rotary evaporator to yield 1.33 g of a clear liquid. The crude product was purified by flash chromatography on silica gel (60 g, EtOAc–heptane, 10:90, 15:85, 20:80, gradient elution). A total of 36 fractions (8 mL) were collected, and fractions 19–31 were combined and concentrated to yield 1.15 g (81%) of **4d** as a clear oil that was determined to be >99% pure by GC and ^{1}H NMR analysis.

Spectral data not previously reported in the literature are given below.

4g

^{1}H NMR (CDCl$_3$): δ = 0.83–0.88 (t, *J* = 6.7 Hz, 3 H), 1.15–1.41 (m, 15 H), 1.52–1.60 (m, 2 H), 1.97–2.15 (m, 1 H), 3.69–3.78 (m, 2 H), 4.05–4.14 (m, 2 H), 4.46–4.50 (t, *J* = 5.2 Hz, 1 H).

^{13}C NMR (CDCl$_3$): δ = 14.0, 22.6, 23.9, 25.8, 29.2, 29.4, 31.8, 35.1, 66.7, 102.3.

4h

^{1}H NMR (acetone-d_6): δ = 1.32–1.40 (m, 1 H), 1.92–2.09 (m, 1 H), 3.80–3.90 (m, 2 H), 4.06–4.12 (m, 2 H), 5.11–5.14 (m, 1 H), 6.17–6.24 (m, 1 H), 6.72–6.77 (d, *J* = 16 Hz, 1 H), 7.23–7.74 (m, 5 H).

^{13}C NMR (acetone-d_6): δ = 27.1, 67.9, 101.9, 128.0, 128.2, 129.4, 130.0, 133.4, 137.8.

4k

^{1}H NMR (acetone-d_6): δ = 0.78 (s, 3 H), 1.23 (s, 3 H), 3.63–3.74 (m, 4 H), 5.41 (s, 1 H), 7.29–7.67 (m, 4 H).

^{13}C NMR (acetone-d_6): δ = 22.6, 24.0, 31.4, 78.6, 101.6, 123.1, 126.8, 130.7, 131.5, 132.9, 143.2.

2-(2-Bromophenyl)-4,7-dihydro-1,3-dioxepine (7a); Typical Procedure

A homogeneous mixture of 2-bromobenzaldehyde (**6a**; 2.00 g, 10.8 mmol), (*Z*)-but-2-ene-1,4-diol (3.43 g, 3.20 mL, 38.9 mmol, 3.6 equiv), and triethyl orthoformate (0.481 g, 0.540 mL, 3.24 mmol, 0.3 equiv) was stirred at r.t. as Bi(OTf)$_3$·xH$_2$O (70.9 mg, 0.108 mmol, 1.0 mol%) was added. The reaction progress was followed by GC. At 1 h 35 min, aq 2 M NaOH (6 mL) was added to the reaction mixture and then stirred for 10 min. The mixture was extracted with Et$_2$O (2 × 30 mL). The combined organic layers were washed with H$_2$O (3 × 20 mL) and brine (20 mL), dried (MgSO$_4$), and concentrated on a rotary evaporator to yield 2.72 g of pale yellow oil. The crude product was purified by flash chromatography on silica gel (150 g, heptane, EtOAc–heptane, 2.5:97.5, and then EtOAc–heptane, 5:95). Following a 400 mL prefraction, 96 fractions (8 mL) were collected, and fractions 68–88 were combined and concentrated to yield 1.54 g (56%) of **7a** as a clear liquid that was determined to be 97% pure by GC and ^{1}H NMR analysis.

^{1}H NMR (acetone-d_6): δ = 4.25–4.45 (m, 4 H), 5.77–5.79 (t, *J* = 1.9 Hz, 2 H), 5.91 (s, 1 H), 7.23–7.90 (m, 4 H).

^{13}C NMR (acetone-d_6): δ = 66.9, 103.1, 123.9, 128.5, 129.4, 130.9, 131.5, 134.3, 139.3.

HRMS-CI: *m/z* calcd for C$_{11}$H$_{12}$BrO$_2$ (M$^+$): 255.00206; found: 255.00131.

7b

^{1}H NMR (acetone-d_6): δ = 4.14–4.45 (m, 4 H), 5.40–5.42 (m, 1 H), 5.73–5.74 (t, *J* = 1.9 Hz, 2 H), 6.28–6.36 (m, 1 H), 6.75–6.82 (m, 1 H), 7.24–7.51 (m, 5 H).

^{13}C NMR (acetone-d_6): δ = 65.5, 102.9, 127.8, 128.1, 129.4, 130.0, 131.4, 133.6, 137.8.

7c

^{1}H NMR (CDCl$_3$): δ = 0.80–0.85 (t, *J* = 6.5 Hz, 3 H), 1.15–1.27 (m, 14 H), 1.55–1.63 (m, 2 H), 4.06–4.37 (m, 4 H), 4.68–4.72 (t, *J* = 5.7 Hz, 1 H), 5.66–5.67 (t, *J* = 1.7 Hz, 2 H).

^{13}C NMR (CDCl$_3$): δ = 14.0, 22.6, 24.7, 29.2, 29.3, 29.4, 29.5, 31.8, 33.5, 64.9, 104.4, 129.7.

HRMS-CI: *m/z* calcd for C$_{14}$H$_{27}$O$_2$ (M$^+$): 227.20111; found: 227.20055.

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