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A Novel and Selective Method for Hydrolysis of Acetals and Ketals

Adam S.-Y. Lee* and C.-L. Cheng

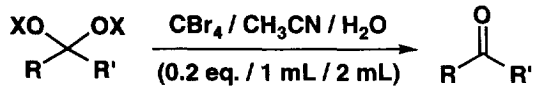
Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137

Abstract: A series of cyclic and acyclic acetals and ketals were hydrolyzed to their corresponding carbonyl compounds by a catalytic amount of CBr_4 (20%) in CH_3CN/H_2O solvent mixture under different energy sources, thermal or ultrasound. The highly chemoselective hydrolysis can be achieved under ultrasonic reaction condition. © 1997 Elsevier Science Ltd.

Introduction

In order to synthesize more complicated molecules, chemists have developed increasingly satisfactory protective groups and effective methods for the formation and cleavage of protected compounds. The search for the selective deprotecting method of acetals and ketals into aldehydes and ketones has been a challenging and rewarding undertaking in organic synthesis.[1,2] Transformation of carbonyl groups into 1,3-dioxolane group is probably the most widely used protective method for carbonyl functionality.[3] Acid catalyzed hydrolysis is the extensively used method for cleavage of acetals and ketals. Acetals and ketals are generally cleaved by protic acids with water as a cosolvent. Several acids such as HCl,[4,5] CH_3CO_2H,[6,7] oxalic acid,[8] *p*-toluenesulfonic acid,[9,10] CF_3CO_2H,[11,12] SiO_2,[13] Dowex-50[14] (acidic resin), Amberlyst-15[15] have been reported for the cleavage of acetals and ketals. Recently, our laboratory reported a novel and highly selective desilylation method which was achieved under ultrasonic conditions.[16] The cleavage of a Si-O bond was performed in a CH_3OH/CCl_4 (v/v=1/1) solution under ultrasound (39 kHz). The results showed that sonication of CCl_4 in CH_3OH led to an acidic (pH 2) reaction condition. We believed that this type of sonochemical reaction conditions[17] can be further extended to the application of hydrolyzing protected carbonyl compounds. Therefore, we investigated the hydrolyzing solvent mixture such as 95%EtOH/CCl_4, H_2O/CCl_4, $H_2O/CHBr_3$ and the deprotection was incomplete or even no hydrolyzed product was obtained. We think that using CBr_4 to replace CCl_4 may generate HBr *in situ* which is more acidic than HCl generated from H_2O/CCl_4. Herewith, we wish to report a novel hydrolyzing method for acetals and ketals (Scheme 1).

Scheme 1



X = CH_3, C_2H_5, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$

Results and Discussions

Previous studies showed that aldehyde acetals when conjugated with electron-withdrawing groups, tends to be slow or even resistent to hydrolyze under acidic condition.[1,15] Therefore, we chose strong electron-withdrawing group substituted *p*-nitrobenzaldehyde as starting material for hydrolyzing investigations. Cyclic (1,3-dioxolane) and acyclic (dimethyl and diethyl) acetals/ketals of *p*-nitrobenzaldehyde and acetophenone were synthesized for the hydrolysis investigations. These acetals and ketals were investigated in a CBr_4 / CH_3CN / H_2O (0.2 eq. / 1 mL / 2 mL) mixture under thermal or ultrasonic reaction conditions.[18] The hydrolysis results are shown in Table 1.

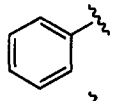
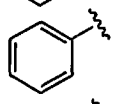
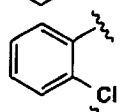
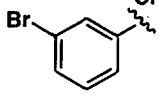
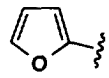
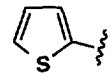
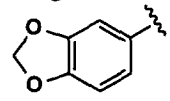
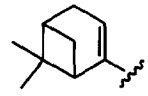
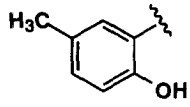
Table 1. Hydrolysis of acetals and ketals

Entry	X	R	R'	Condition[a]	Yield
1	$-CH_2CH_2-$	O_2N–	H	A (6h) B (6h)	92% N.R.[b]
2	$-CH_2CH_2-$	O_2N–	CH_3	A (6h) B (6h)	95% N.R.[b]
3	$-CH_3$	O_2N–	H	A B (4h)	97% N.R.[b]
4	$-CH_3$	O_2N–	CH_3	A B (4h)	97% N.R.[b]
5	$-CH_2CH_3$	O_2N–	H	A B	96% 25%[c]
6	$-CH_2CH_3$	O_2N–	CH_3	A B B (4h)	97% 43%[c] 97%

a. The typical (nonindicated) reaction time is 2 hours.
Condition A: refluxed at 80 ^{0}C.
Condition B: sonicated in ultrasonic cleaning bath (39 kHz).
b. No reaction and recovery of starting material.
c. The rest starting material was recovered.

All the acetals and ketals (Table 1) can be hydrolyzed in $CBr_4/CH_3CN/H_2O$ mixture under thermal reaction conditions (Condition A). It appears that the 2-(*p*-nitrophenyl)-1,3-dioxolanes and acyclic dimethyl acetal (Table 1, Entries 1-4) were resistant even at a prolonged reaction time under the sonochemical reaction conditions (Condition B). Interestingly, these compounds can be easily hydrolyzed in the same reaction mixture under thermal conditions. Our observations show that selective hydrolysis may be achieved in $CBr_4/CH_3CN/H_2O$ reaction system under ultrasound. Therefore, we are interested in the investigation of hydrolysis selectivities[12,19-21] for 1,3-dioxolane under sonochemical reaction conditions. A series of 1,3-dioxolanes were synthesized and investigated under 2 hours sonochemical reaction condition (Condition B). The sonochemical hydrolysis results of 1,3-dioxolane are shown in Table 2.

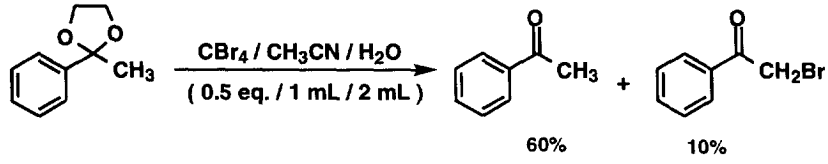
Table 2. Sonochemical hydrolysis of 1,3-dioxolanes[a]

Entry	X	R	R'	Yield
1	$-CH_2CH_2-$		H	74%[b]
2	$-CH_2CH_2-$		CH_3	93%
3	$-CH_2CH_2-$		H	20% 95%[c]
4	$-CH_2CH_2-$		H	93%
5	$-CH_2CH_2-$		H	81%
6	$-CH_2CH_2-$		H	91%
7	$-CH_2CH_2-$		H	94%
8	$-CH_2CH_2-$		H	99%
9	$-CH_2CH_2-$		CH_3	98%[d]
10	$-CH_2CH_2-$	$n\text{-}C_5H_{11}$	C_2H_5	76%[b]

a. The typical reaction time is 2 hours.
b. The yield is low because the product is highly volatile.
c. The yield was achieved under 6 hours sonication.
d. The reaction is occured under a 2mL CH_3CN / 4mL H_2O / 0.4 eq CBr_4 reaction condition.

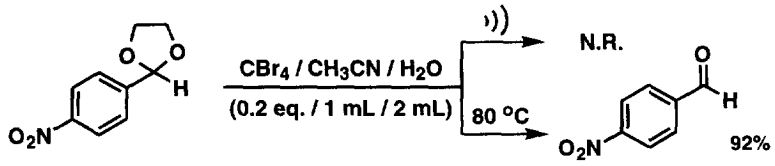
The results showed that 1,3-dioxolanes without strong electron-withdrawing groups substituted can be easily hydrolyzed under sonochemical reaction conditions. The weaker electron-withdrawing substituted carbonyl compound such as *o*-chlorobenzaldehyde acetal also shows slower hydrolyzing rate under ultrasonic reaction condition (Table 2, Entry 3). The proper ratio among $CBr_4/CH_3CN/H_2O$ was investigated and 0.2 eq. CBr_4/1mL CH_3CN/2mL H_2O is the best combination for sonochemical hydrolysis reaction. The 20% catalytic amount of CBr_4 is adequate enough for the hydrolysis of 1,3-dioxolanes. It should be noted that a side product, α-bromination compound, will be generated when more than 50% CBr_4 was reacted with ketal. A solution of 1,3-dioxolane ketal (Table 2, Entry 2) was sonicated with 0.5 equivalent of CBr_4 in CH_3CN/H_2O mixture for 3 hours and the hydrolyzed product was produced in 60% yield with a 10% yield of α-brominated compound (Scheme 2).

Scheme 2



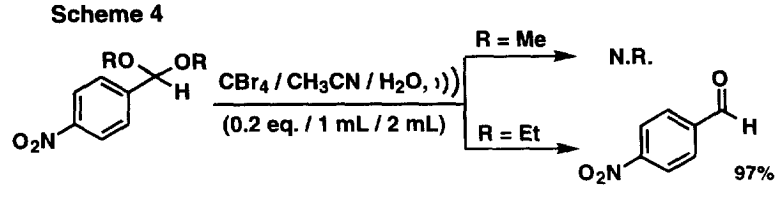
When strong electron-withdrawing group exists, the hydrolyzing rate shows dramatically decreasing which is resistent to hydrolyze under ultrasonic reaction conditions (Table 1, Entries 1-4). An efficient and highly chemoselective hydrolysis was observed in the same reaction mixture under different energy sources (Scheme 3).

Scheme 3



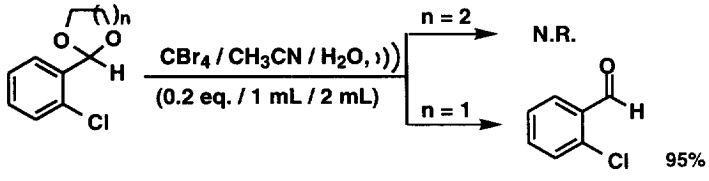
Our observations show that selective hydrolysis can be achieved for electron-withdrawing group substituted 1,3-dioxolane under ultrasonic energy source. Therefore, we are interested in the investigations of hydrolyzing selectivities for acyclic nitro-substituted acetals under ultrasonic reaction condition. The dimethyl and diethyl acetals of *p*-nitrobenzaldehyde were synthesized and investigated (Table 1, Entries 3-6). Suprisingly, *p*-nitrobenzaldehyde diethyl acetal was sonicated for 4 hours and a 97% yield of *p*-nitrobenzaldehyde was obtained whereas the dimethyl acetal was resistent under sonochemical reaction condition. An amazing selective hydrolysis was afforded between acyclic dimethyl and diethyl acetals and this type of selectivity has not been reported before (Scheme 4).

Scheme 4



The relative rate of acidic hydrolysis of 1,3-dioxolane (5-member ring) and 1,3-dioxane (6-member ring) acetals has been studied and indicated that hydrolysis of 1,3-dioxolane is faster than 1,3-dioxane.[22] Our observations show that weaker electron-withdrawing group substituted acetal such as *o*-chlorobenzaldehyde acetal has slower hydrolyzing rate under ultrasonic reaction condition (Table 2, Entry 3). Therefore, we are interested in the investigations of hydrolysis between the ring size of acetals such as *o*-chlorobenzaldehyde 1,3-dioxolane and 1,3-dioxane. The highly chemoselective hydrolysis between the ring size of 1,3-dioxolane and 1,3-dioxane also were observed as expected. *o*-Chlorophenyl-1,3-dioxolane was sonicated for 6 hours and a 95% yield of *o*-chlorobenzaldehyde was obtained whereas the 1,3-dioxane was resistent under ultrasonic reaction condition (Scheme 5). It should be noted that *o*-chlorophenyl-1,3-dioxane was hydrolyzed to its corresponding aldehyde in a 99% yield after 3 hours refluxing (condition A).

Scheme 5



All the cyclic and acyclis acetals/ketals (Table 1 and 2) can be hydrolyzed under thermal reaction condition and the selective hydrolysis is achieved for the strong electron-withdrawing group substituted acetal under ultrasonic reraction condition. The mechanism for selective hydrolysis of acetals under sonochemical reaction condition is not clear. Functionalities such as alcohol, ester and amide are stable under the sonochemical reaction conditions.[23] Further application in the hydrolysis of tetrahydropyranyl ether and methoxymethyl ether is underway.

Experimental Section

General

The ^{1}H-NMR (proton nuclear magnetic resonance) spectra were recorded at 300 MHz (Bruker-AC300P) with deuteriochloroform ($CDCl_3$, Aldrich 99.8 atom% D) as the solvent and the internal standard. The ^{13}C-NMR (carbon nuclear magnetic resonance) spectra were recorded at 75.5 MHz (Bruker-AC300P) with $CDCl_3$ as the solvent and the internal standard. Chemical shifts are reported in parts per million and resonance patterns are reported with the notations of either s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants (J) are reported in hertz (Hz). Mass spectra (MS) were recorded on a JEOL SX-102A and VG 70-250S spectrophotometers and are reported in *m/e* units for the most abundant peaks. All experiments were carried out under a nitrogen atmosphere which was dried primarily by passing through a column of potassium hydroxide (KOH) layered with calcium sulfate ($CaSO_4$). Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and recirculated prior to use. Carbon tetrachloride, methylene chloride, hexane and ethyl acetate were distilled from calcium hydride. Methanol was distilled from magnesium turning and recirculated prior to use.

Thin-layer chromatography (TLC) analysis was performed on a plastic plate (or aluminum sheet) precoated with silica gel (Merck, 5554 Silica gel 60F254). Visualization was accomplished by UV light or developed by spraying with a 10% phosphomolybdic acid ethanol solution. Column chromatography was performed using silica gel (Merck 230-400 mesh) and ethyl acetate/hexane mixtures as the eluent. Spectral grade purification by high performance liquid chromatography (HPLC) was carried out using a Rheodyne 7000 sample injector, Jasco PU-980 intelligent pumps, Jasco RI-930 Refractive Index Detector and Phenomenex columns (Spherex 10 Silica).

All aldehydes and ketones (Table 1 and 2) were purchased from Aldrich, Merck and Riedel-deHaen and all were used directly without further purification. All acetals and ketals in Table 1 and 2 were synthesized by the previously reported method.[7, 24-26] Hydrolysis of these acetals and ketals were investigated under the typical procedures shown below and the yields are the isolated yields after chromatography.

Typical Procedure for the Acetal and Ketal Hydrolysis Reaction

Condition A

A solution of acetal or ketal (1.0 mmol), CBr_4 (0.2 mmol) in CH_3CN (1 mL / mmol) and H_2O (2 mL / mmol) is refluxed at 80 °C[27] for 2-6 hours. The solution was cooled to room temperature and poured into a saturated $NaHCO_3$ solution (10 mL) and then extracted with diethyl ether (3 x 10 mL). The organic layer is collected, washed with brine (10 mL), dried with $MgSO_4$, filtered, and the organic solvent was removed under reduced pressure. Further purification was achieved on a flash chromatograph with silica gel and ethyl acetate/hexane.

Condition B

A solution of acetal or ketal (1.0 mmol), CBr_4 (0.2 mmol) in CH_3CN (1 mL / mmol) and H_2O (2 mL / mmol) is sonicated in a commercial ultrasonic cleaning bath[28] (Crest 575-D, 39 kHz) at around 45 °C. After the sonication, the solution was added to a saturated $NaHCO_3$ solution (10 mL) and then extracted with diethyl ether (3 x 10 mL). The organic layer is collected, washed with brine (10 mL), dried with $MgSO_4$, filtered, and the organic solvent was removed under reduced pressure. Further purification was achieved on a flash chromatograph with silica gel and ethyl acetate/hexane.

2-(4-Nitrophenyl)-1,3-dioxolane (Table 1, Entry 1)

^{1}H-NMR: δ 4.00-4.20 (4H, m), 5.84 (1H, s), 7.60 (2H, d, J=8.8), 8.18 (2H, d, J=8.8). ^{13}C-NMR: δ 65.3, 102.1, 123.8, 127.3, 144.9, 148.3.

2-Methyl-2-(4-nitrophenyl)-1,3-dioxolane (Table 1, Entry 2)

^{1}H-NMR: δ 1.64 (3H, s), 3.72-3.83 (2H, m), 3.99-4.14 (2H, m), 7.65 (2H, d, J=8.8), 8.17 (2H, d, J=8.8). ^{13}C-NMR: δ 27.4, 64.7, 108.1, 123.5, 126.4, 147.7, 150.6.

4-(Dimethoxymethyl)nitrobenzene (Table 1, Entry 3)

^{1}H-NMR: δ 3.22 (6H, s), 5.35 (1H, s), 7.51 (2H, d, J=8.7), 8.06 (2H, d, J=8.7). ^{13}C-NMR: δ 52.3, 101.3, 122.9, 127.5, 144.9, 147.6. MS: m/z 196 (M-1, 3), 166 (base), 120 (34), 108 (18), 91 (12), 75 (17), 46 (13), 29 (17).

4-(1,1-Dimethoxyethyl)nitrobenzene (Table 1, Entry 4)

^{1}H-NMR: δ 1.53 (3H, s), 3.19 (6H, s), 7.67 (2H, d, J=9.0), 8.20 (2H, d, J=9.0). ^{13}C-NMR: δ 25.8, 49.1, 101.2, 123.4, 127.4, 147.5, 150.2.

4-)Diethoxymethyl)nitrobenzene (Table 1, Entry 5)
^{1}H-NMR: δ 1.21 (6H, t, J=7.0), 3.48-3.65 (4H, m), 5.54 (1H, s), 7.62 (2H, d, J=8.6), 8.16 (2H, d, J=8.6). ^{13}C-NMR: δ 15.0, 61.2, 100.1, 123.2, 127.6, 146.1, 147.8. MS: m/z 226 (M+1, 13), 108 (base), 106 (11), 153 (6), 152 (63), 105 (10), 77 (13), 29 (18).

4-(1,1-Diethoxyethyl)nitrobenzene (Table 1, Entry 6)
^{1}H-NMR: δ 1.21 (6H, t, J=7.1), 1.54 (3H, s), 3.26-3.38 (2H, m), 3.42-3.55 (2H, m), 7.69 (2H, d, J=8.9), 8.17 (2H, d, J=8.9). ^{13}C-NMR: δ 15.2, 26.8, 57.0, 100.7, 123.2, 127.3, 147.4, 151.1.

2-Phenyl-1,3-dioxolane (Table 2, Entry 1)
^{1}H-NMR: δ 3.90-4.20 (4H, m), 5.86 (1H, s), 7.35-7.48 (3H, m), 7.49-7.58 (2H, m). ^{13}C-NMR: δ 65.1, 103.5, 126.4, 128.2, 128.8, 137.9. MS: m/z 150 (M, 11), 149 (base), 106 (11), 105 (95), 77 (58), 51 (34), 43 (23), 31 (19), 30 (28).

2-Methyl-2-phenyl-1,3-dioxolane (Table 2, Entry 2)
^{1}H-NMR: δ 1.67 (3H, s), 3.17-3.85 (2H, m), 3.95-4.08 (2H, m), 7.25-7.39 (3H, m), 7.48-7.56 (2H, m). ^{13}C-NMR: δ 27.5, 64.3, 108.7, 125.1, 127.6, 128.0, 143.3. MS: m/z 165 (M+1, 10), 164 (M, 2), 149 (base), 133 (17), 105 (65), 87 (61), 77 (58), 43 (54), 29 (26).

2-(3-Bromophenyl)-1,3-dioxolane (Table 2, Entry 4)
^{1}H-NMR: δ 3.97-4.15 (4H, m), 5.79 (1H, s), 7.25 (1H, t, J=7.7), 7.40 (1H, dt, J=7.7, 1.4), 7.47-7.51 (1H, ddd, J=7.7, 1.9, 1.4), 7.64 (1H, dd, J=1.9, 1.4). ^{13}C-NMR: δ 65.3, 102.7, 122.5, 125.1, 129.5, 129.9, 132.2, 140.4.

2-(2-Furyl)-1,3-dioxolane (Table 2, Entry 5)
^{1}H-NMR: δ 3.92-4.25 (4H, m), 5.91 (1H, s), 6.34 (1H, dd, J=3.2, 1.8), 6.43 (1H, d, J=3.2), 7.40 (1H, d, J=1.8). ^{13}C-NMR: δ 65.0, 97.6, 108.6, 110.0, 143.0, 151.0.

2-(2-Thienyl)-1,3-dioxolane (Table 2, Entry 6)
^{1}H-NMR: δ 3.80-4.20 (4H, m), 6.12 (1H, s), 6.99 (1H, dd, J=5.0, 3.5), 7.18 (1H, d, J=3.5), 7.33 (1H, dd, J=5.0, 1.2). ^{13}C-NMR: δ 65.0, 100.1, 126.1, 126.2, 126.5, 141.6. MS: m/z 156 (M, 53), 155 (66), 111 (79), 97 (34), 96 (30), 84 (base), 73 (22), 39 (25), 29 (24).

2-(3,4-Methylenedioxyphenyl)-1,3-dioxolane (Table 2, Entry 7)
^{1}H-NMR: δ 3.95-4.20 (4H, m), 5.71 (1H, s), 5.95 (2H, s), 6.79 (1H, d, J=8.0), 6.91-6.98 (2H, m).

2-Myrtenyl-1,3-dioxolane (Table 2, Entry 8)
^{1}H-NMR: δ 0.83 (3H, s), 1.18 (1H, d, J=8.7), 1.29 (3H, s), 2.07-2.13 (1H, br), 2.19-2.50 (4H, m), 3.80-4.02 (4H, m), 5.13 (1H, s), 5.73 (1H, s). ^{13}C-NMR: δ 21.1, 26.0, 31.3, 31.7, 37.8, 40.9, 41.2, 65.0, 65.1, 104.6, 124.0, 144.8.

2-(2-Hydroxy-5-methylphenyl)-2-methyl-1,3-dioxolane (Table 2, Entry 9)
^{1}H-NMR: δ 1.69 (3H, s), 2.26 (3H, s), 3.82-3.95 (2H, m), 4.02-4.18 (2H, m), 6.76 (1H, d, J=8.2), 7.00 (1H, d, J=8.2), 7.09 (1H, s), 8.01 (1H, s).

2-Ethyl-2-pentyl-1,3-dioxolane (Table 2, Entry 10)
^{1}H-NMR: δ 0.84 (3H, t, J=6.7), 0.85 (3H, t, J=7.4), 1.14-1.38 (6H, m), 1.48-1.64 (4H, m), 3.86 (4H, s). ^{13}C-NMR: δ 7.9, 13.9, 22.5, 23.4, 29.8, 32.1, 36.6, 64.8, 112.0. MS: m/z 171 (M-1, 1), 143 (77), 101 (base), 86 (9), 71 (8), 57 (20), 43 (12), 29 (14).

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28. The bath should be filled with water containing 5% detergent. In our laboratory, we used Decon 90 which permits much more even cavitation in bath water.

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