Phosphonium salts and aldehydes from the convenient, anhydrous reaction of aryl acetals and triphenylphosphine hydrobromide

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Abstract

The reactions of aryl acetals/ketals and triphenylphosphine hydrobromide gave the corresponding aldehydes/ketones and alkyl phosphonium bromides. This reaction was applied to convert acetals/ketals to the corresponding aldehydes/ketones under an anhydrous and convenient condition (50 °C, 5 min, up to 90% yield), and acid sensitive functional groups were compatible.

Keywords: Acetal, phosphonium salt, protecting group, anhydrous deprotection.

Introduction

Preparation and removal of acetals/ketals are often encountered in organic synthesis since the two functionalities are the primary protecting groups for aldehydes and ketones.[1] The deprotection of acetals/ketals is usually achieved by acidic, aqueous hydrolysis.[1,2] However, such conditions may cause problems for moisture- or acid-sensitive substrates. Several reagents, such as (trimethylsilyl)-bis(fluorosulfuryl)imide,[3] dimethyldioxirane (DMDO),[4] iodine,[5] trimethylsilyl triflate,[6] acetyl chloride/zinc chloride,[7] phosphorus triiodide,[8] and photocleavage,[9] have been developed to accomplish the deprotection under an anhydrous condition. We have found that the reaction of aryl acetals with the stable, non-hygroscopic, metal-free and commercially available salt, triphenylphosphine hydrobromide (PPh$_3$•HBr)[10], provides the corresponding aldehydes/ketones and phosphonium salts in good yields. This paper reports our work to develop this reaction as a convenient and selective anhydrous deprotection method for aryl acetals and ketals (Equation 1).
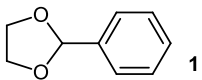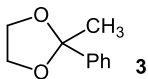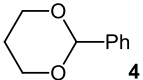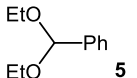
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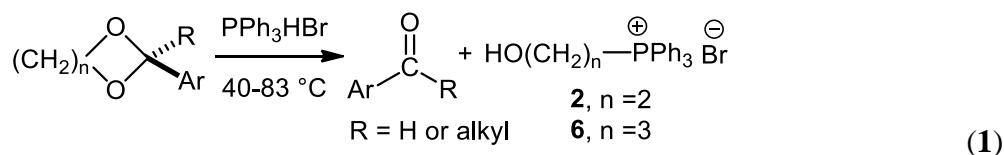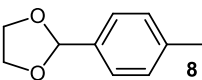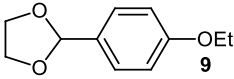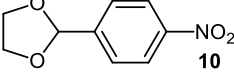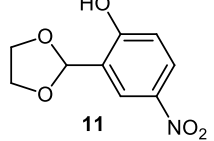
Results and Discussion

We previously reported that PPh$_3$•HBr was able to cleave benzyl ethers,[11] which prompted us to apply this reagent to other functional groups. It was interesting to observe that aryl acetals/ketals were also susceptible to PPh$_3$•HBr, but in a different reaction pathway. The reaction mixture of 2-phenyl-1,3-dioxolane (**1**) and PPh$_3$•HBr, refluxed in dichloromethane for 3 h, provided the two products: benzaldehyde (68%) and (2-hydroxyethyl)triphenylphosphonium bromide (**2**, 73%), which were isolated and characterized. The spectroscopic data (^{1}H, ^{13}C, ^{31}P NMR) and mass analysis of this ionic product were consistent with those of (2-hydroxyethyl)triphenylphosphonium bromide.[12] The separation of the products could be easily achieved by adding diethyl ether to the concentrated product mixture, and the phosphonium salt precipitated.

To further improve the efficiency of this protocol, we applied microwave assisted heating and shortened the reaction time to 5 min at 50 ℃ in a sealed tube. Alternatively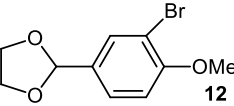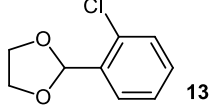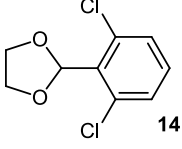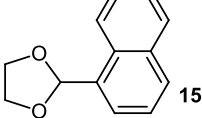, conventional heating using 1,2-dichloroethane (bp 83 ℃) also reduced the reaction time to 30 min. The results for the deprotection of some aryl acetals/ketals by PPh$_3$•HBr were summarized in Table 1. The reaction of 2-methyl-2-phenyl-1,3-dioxolane (**3**) provided the same salt **2** and acetophenone, showing that this reaction pathway is general for both aryl acetals and ketals (entry 2).

The six-membered 2-phenyl-1,3-dioxane (**4**) generated (3-hydroxypropyl)triphenyl-phosphonium bromide (**6**,[13] 84%, entry 3). The acyclic acetal **5** gave ethyltriphenylphosphonium bromide (**7**,[14] 66%, entry 4), in addition to the benzaldehyde. Both electron donating (entries 5, 6 and 9) and withdrawing groups (entries 7, 8, 10 and 11) on the aromatic ring were acceptable for this reaction, although the substrates with the electron withdrawing nitro group gave the lower yields. The non-reducing nature of PPh$_3$•HBr is beneficial for transformations involving the reducing agent sensitive compounds, such as those with nitro or bromo- substituents. 2,6-Dichlorophenyl acetal **14** and naphthyl acetal **15** also underwent the reaction smoothly (entries 11 and 12).

Table 1

Entry	Reactant	Yield of aldehyde/ketone (%)[a,b]
1	**1**	82(73)[c]
2	**3**	77
3	**4**	67(84)[c]
4	**5**	73(66)[c]
5	**8**	77
6	**9**	73
7	**10**	66
8	**11**	61
9	**12**	73
10	**13**	74
11	**14**	76
12	**15**	84

[a] 50 ºC, 5 min.
[b] Isolated yields after column chromatography.
[c] Yield of the corresponding phosphonium salt.

The anhydrous reaction conditions and water free work-up procedures are favorable for the acetals/ketals bearing acid and moisture sensitive functional groups (Equation 2, Table 2). We found that common protecting groups for hydroxyls, such as the silyl groups (TBDPS and TBS, entries 1-2) and the substituted methyl ethers (MOM and Bn, entries 3-4) remained intact under this protocol. In contrast to the aryl acetal, the aliphatic, 1,3-dioxolane moiety of **20a** was also compatible with triphenylphosphine hydrobromide (entry 5). The results from the substrates **19a** and **20a** demonstrated that the aryl acetals are far more reactive to PPh₃•HBr than the benzyl ether and the aliphatic acetal. This trend is consistent with the relative hydrolysis rate of aryl *versus* alkyl acetals, which suggests that the formation of the intermediate, oxocarbenium ion, is the rate determining step for both reactions (*vide infra*).[15]
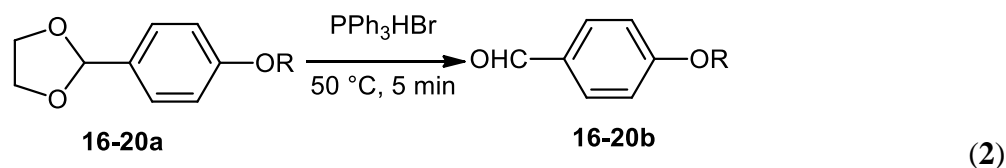

$$16\text{-}20a \qquad \xrightarrow[\text{50 °C, 5 min}]{\text{PPh}_3\text{HBr}} \qquad 16\text{-}20b \tag{2}$$
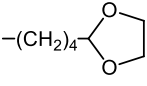
Table 2. Reactions of aryl acetals with protecting groups

Entry	Reactant	Product	Yield(%)[a,b]
1	R = -Si(^{t}Bu)Ph₂ (TBDPS), **16a**	**16b**	(89)
2	R = -Si(^{t}Bu)Me₂ (TBS), **17a**	**17b**	81
3	R = -CH₂OCH₃ (MOM), **18a**	**18b**	77
4	R = Bn, **19a**	**19b**	68
5	R = $-(CH_2)_4$, **20a**	**20b**	90

[a] 50 ºC, 5 min.
[b] Isolated yields after column chromatography.

4-Substituted dioxolanes **21** and **22** were prepared to further explore this reaction.[16] In addition to benzaldehyde, (2-hydroxypropyl)- and (2-hydroxy-2-phenylethyl)-triphenylphosphonium salts **23**[17] and **24**[18] (Equation 3) were produced. However, the other possible phosphonium salts, **25**, with a primary hydroxyl group, were not observed (Scheme 1). These results indicated that triphenylphosphine only attacked the sterically less hindered primary carbon, rather than the secondary carbon or the sp^2 carbon, of the intermediate oxocarbenium ion. The latter pathway was observed in the reactions of the less hindered triethylphosphine.[19] This unique property of PPh₃•HBr could be applied to prepare the corresponding phosphonium salts,

such as **23** and **24**, directly from the aryl acetals/ketals, rather than the sequence of deprotection, bromination and the formation of phosphonium salt, as shown in the reported syntheses.[20]

$$R = CH_3, \textbf{21}$$
$$Ph, \textbf{22}$$

$$R = CH_3, \textbf{23}, 69\%$$
$$Ph, \textbf{24}, 67\%$$

72-74%

(3)
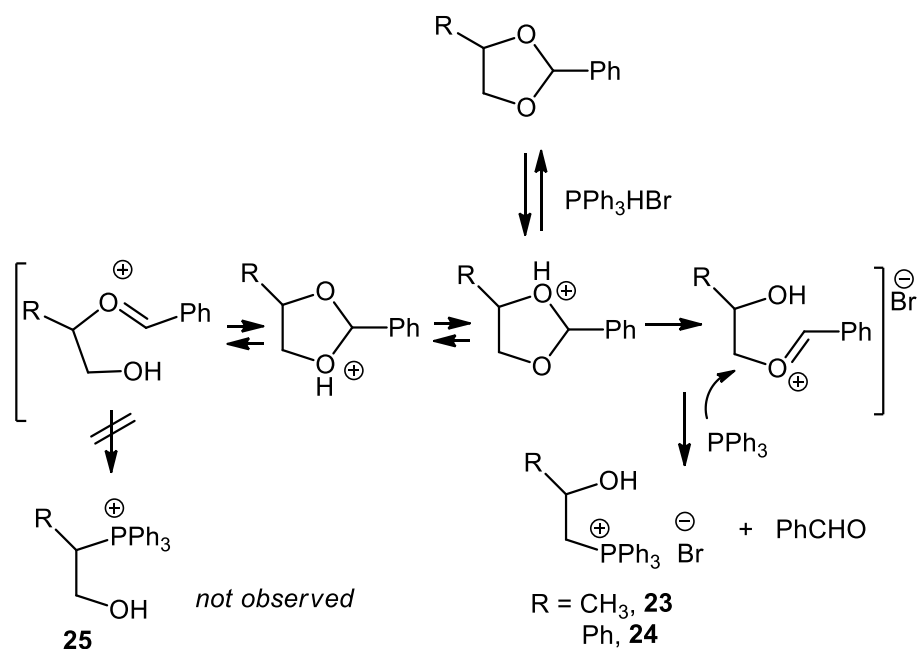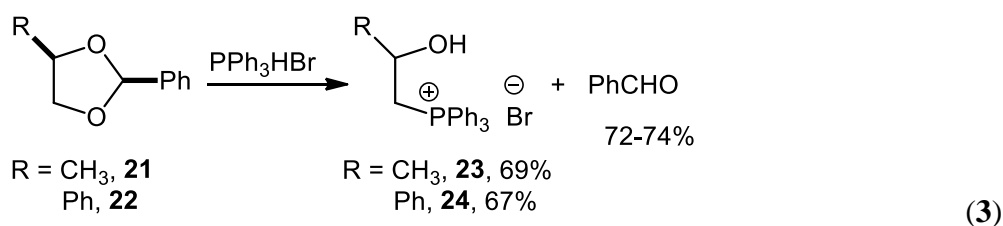
Scheme 1. Proposed reaction mechanism for the reactions of the aryl acetals and PPh₃•HBr.

Conclusions

To our knowledge, the reaction of aryl acetals/ketals and triphenylphosphine hydrobromide was only briefly described.[19] We developed this reaction as a convenient, deprotection method for aryl acetals/ketals and a direct preparation of the corresponding phosphonium salts. Its efficiency, mildness and anhydrous conditions could be useful for substrates with these concerns. The formation of the phosphonium salts is selective when the substituted dioxolanes are applied, and this process is different from that of triethylphosphine hydrobromide.

Experimental Section

General. All purchased chemicals were used without further purification. THF was distilled from sodium benzophenone ketyl. ^{1}H and ^{13}C NMR spectra were obtained on 300 MHz spectrometers and referenced to TMS or residual CHCl$_3$. Analytical TLC was carried out using aluminum-backed 0.2 mm silica gel 60 F254 plates. Column chromatography was conducted using 230-400 mesh silica gel.

Compounds **1**,[21] **3**,[22] **4**,[23] **5**,[24] **8**,[24] **10**,[25] **11**,[26] **12**,[27] **13**[28], **15**[29], **13a-b**,[30] **14a-b**,[23] **15b**,[31] **16b**,[32] **18**,[16] **19**,[16,33] were known, and were prepared according to the general procedure.

Standard procedure for the acetal deprotection. A solution of acetal (0.66 mmol), triphenylphosphine hydrobromide (0.73 mmol) in dry dichloromethane (0.5 mL) was placed in a reaction tube (10 mL, for microwave reaction). The tube was capped and heated to 50 ℃ for 5 minutes in a microwave oven (CEM Discover). After cooling to room temperature, the reaction mixture was concentrated under vacuum. The alkyl phosphonium salts precipitated after adding diethyl ether, and the aldehyde was harvested after concentrating the filtrate. Alternatively, the separation of the two products could be achieved by flash column chromatography.

2-(2,6-Dichlorophenyl)-1,3-dioxolane (14). A mixture of 2,6-dichlorobenzaldehyde (0.5 g, 2.86 mmol), ethylene glycol (0.8 g, 11.6 mmol) and *p*-TsOH.H$_2$O (54 mg, 0.28 mmol) in dry toluene (20 mL) was equipped with a Dean-Stark apparatus and heated to reflux for 12 h. After cooling the mixture to room temperature, added 10 mL of saturated aq. Sodium bicarbonate solution and extracted with ethyl acetate (2 × 25 mL) combined organic layers were washed with brine (20 mL), dried over sodium sulfate. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (5%, ethyl acetate: hexanes, trace amount of triethylamine) to give the title compound (0.38 g, 2.17 mmol, 63%) as a colorless solid. Mp 44.5-46.0 ℃; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.97-4.13 (m, 4H), 6.45 (s, 1H), 7.16-7.30 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 65.9, 101.0, 129.5, 130.6, 130.8, 136.0.

2-(4-(Methoxymethoxy) phenyl)-1,3-dioxolane (18a). A solution of 4-(1,3-dioxolan-2-yl)phenol (0.37 g, 2.23 mmol) and *N,N*-disopropylethylamine (1.44 g, 1.9 mL, 11.13 mmol) in 5 mL dry dichloromethane was cooled to 0 ℃. A solution of methoxymethyl chloride (0.36 g, 0.34 mL, 4.45 mmol) and *N,N*-disopropylethylamine (1.44 g, 1.9 mL, 11.13 mmol) in 5 mL dry dichloromethane was added slowly over 10 min. The reaction mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was diluted with dichloromethane (10 mL), washed with saturated aqueous ammonium chloride (5 mL), saturated aqueous sodium bicarbonate (5 mL), water (5 mL), brine (5 mL). The combined organic layers were dried over sodium sulfate and the solvents were removed under reduced pressure. The crude mixture was purified by flash column chromotography (10%, ethyl acetate: hexanes, trace amount of triethylamine). The title compound was isolated (0.32 g, 1.52 mmol, 68%) as colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.37 (s, 3 H), 3.91-3.93 (m, 2H), 4.00-4.05 (m, 2H), 5.08 (s, 2H), 5.67 (s, 1H), 6.95 (d, 8.7 Hz, 2H), 7.31 (d, 8.7 Hz, 2H);^{13}C NMR (75 MHz, CDCl$_3$) □δ 55.9,

65.2, 94.2, 103.50, 115.9, 127.8, 131.2, 157.9. HRMS (FAB) calcd. for [M+H$^+$] (C$_{11}$H$_{15}$O$_4$), 211.0970; found 211.0970.

2-(4-(Benzyloxy) phenyl)-1,3-dioxolane (19a). A mixture of 4-(benzyloxy)benzaldehyde (0.5 g, 2.36 mmol), ethylene glycol (0.9 g, 14.13 mmol) and *p*-TsOH.H$_2$O (36 mg, 0.19 mmol) in dry benzene (15 mL) was equipped with a Dean-Stark apparatus and heated to reflux for 24h. After cooling the mixture to room temperature, added 10 mL of saturated aq. Sodium bicarbonate solution and extracted with ethyl acetate (2 × 25 mL) combined organic layers were washed with brine (20 mL), dried over sodium sulfate. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (20%, ethyl acetate: hexanes, trace amount of triethylamine) to give the title compound (0.40 g, 1.57 mmol, 67%) as a colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.97-4.13 (m, 4H), 5.06 (s, 2H), 5.74 (s, 1H) 6.94-6.98 (m, 2H), 7.29-7.42 (m, 7H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 65.2, 70.0, 103.6, 115.2, 117.7, 127.4, 127.8, 127.9, 128.5, 136.8, 159.5.[34]

2-(4-(4-(1,3-Dioxolan-2-yl)butoxy)phenyl)-1,3-dioxolane (20a). A suspension of 4-(5-oxopentyloxy)benzaldehyde (0.5 g, 2.42 mmol), ethylene glycol (0.9 g, 14.54 mmol) and *p*-TsOH·H$_2$O (37 mg, 0.19 mmol) in dry toluene (15 mL) was equipped with a Dean-Stark apparatus and heated to reflux for 12h. After cooling the mixture to room temperature, added 10 mL of saturated aq. sodium bicarbonate solution and extracted with ethyl acetate (2 × 20 mL), combined organic layers were washed with brine (20 mL), dried over sodium sulfate. Solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (20%. ethyl acetate: hexanes, trace amount of triethylamine) to give the title compound (0.506 mg, 1.72 mmol, 73%) as a colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.67-1.82 (m, 6H), 3.81-4.09 (m, 10H), 4.85 (t, 9 Hz, 3H), 5.71 (s, 1H), 6.85 (d, 8.7 Hz, 2H), 7.35 (d, 4.35 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.5, 29.0, 33.4, 64.8, 65.2, 67.7, 103.7, 104.3, 114.2, 127.8, 129.7, 159.8. HRMS (FAB) calcd. for [M+H$^+$] (C$_{16}$H$_{23}$O$_5$), 295.1546; found 295.1538.

4-(4-(1,3-Dioxolan-2-yl)butoxy)benzaldehyde (20b). The standard procedure for the deprotection was followed. Starting with **20a** (100.1 mg, 0.34 mmol), **20b** was isolated after silica gel column chromatography (20% Ethyl acetate: Hexane, trace amount of triethylamine), as a colorless oil, (61.2 mg, 0.24 mmol, 72%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.72-1.89 (m, 6H), 3.81-4.05 (m, 6H), 4.86 (t, 4.8 Hz, 3H), 6.95 (d, 8.7 Hz, 2H), 7.79 (d, 8.7 Hz, 2H), 9.85 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$), 20.5, 28.9, 33.4, 64.9, 68.1, 104.3, 114.7, 129.7, 132, 164.1, 190.8. HRMS (EI) calcd. for [M$^+$] (C$_{14}$H$_{18}$O$_4$) 250.1205, found 250.1206.

2,4-Diphenyl-1,3-dioxolane (22). To a solution of 1-phenylethane-1,2-diol (500 mg, 3.62 mmol) and benzaldehyde (576 mg, 5.42 mmol) in dry dichloromethane (6 mL) was added *p*-TsOH·H$_2$O (63 mg, 0.09 mmol). The reaction mixture was stirred at room temperature for 15 h, then diluted with 10 mL dichloromethane and washed with 5 mL of saturated aqueous sodium bicarbonate solution, washed with 5 mL of brine solution. The organic layer was dried over sodium sulfate and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (2%, ethylacetate: hexanes with trace amount of triethylamine) to give

the title compound (0.46 g, 2.0 mmol, 44%) ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.95 (m, 1H), 4.38 (t, 7.1 Hz, 1H), 5.21 (t, 7.1 Hz, 1H), 6.02 (s, 1H), 7.32-7.62 (m, 10 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 72.2, 78.8, 104.6, 126.4, 126.7, 128.2, 128.4, 128.5, 129.3, 137.4, 139.0.

Acknowledgements

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