JOC*Note*

Tetrabutylammonium Tribromide (TBATB) as An Efficient Generator of HBr for an Efficient Chemoselective Reagent for Acetalization of Carbonyl Compounds†

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Abstract: Acyclic and cyclic acetals of various carbonyl compounds were obtained in excellent yields under a mild reaction condition in the presence of trialkyl orthoformate and a catalytic amount of tetrabutylammonium tribromide (TBATB) in absolute alcohol. Chemoselective acetalization of an aldehyde in the presence of ketone, unsymmetrical acetal formation, shorter reaction times, mild reaction conditions, the stability of acid-sensitive protecting groups, high efficiencies, facile isolation of the desired products, and the catalytic nature of the reagent make the present methodology a practical alternative.

During a multistep synthesis, a carbonyl group may have to be protected against an attack by various reagents such as nucleophiles, oxidants, basic, catalytic, or hydride reducing agents, including organometallic reagents.[1a−d] Acetals are generally formed under acidic conditions, and water formed during a reaction is removed either by physical or chemical methods.[1c] Orthoesters such as triethyl orthoformate are used as one of the chemical methods for the removal of water, which reacts with the water formed by the reaction of aldehyde and ketone with an alcohol to form ethanol and ethylformate, resulting in the equilibrium shifting to the right.[1c] Methods are available for the conversion of carbonyl groups in aldehydes and ketones to their corresponding acetals using trialkyl orthoformates in the presence of acid catalysts such as HCl,[2a] $FeCl_3$,[2b] Amberlyst-15,[2c] $ZrCl_4$,[2d] DDQ,[2e] NBS,[2f,g] and $Sc(NTf_2)_3$.[2h] Unfortunately, many of these procedures often require a large excess of reagents, longer reaction times, drastic reaction conditions, and moisture-sensitive and expensive reagents. Also, some of these reagents do not always prove to be satisfactory for the acetalization of cyclic and aromatic ketones. Previously, tetrabutylammonium tribromide (TBATB) has been used as a brominating agent,[3a−d] for the cleavage of *tert*-butyldimethylsilyl ethers[4] and dithioacetals,[5] and the pyranylation−depyranylation of alcohols.[6] The identification of tetrabutylammonium tribromide as a catalytic, mild, and chemoselective reagent for the acetalization of carbonyl compound is the basis of this investigation.

In this note, we report a mild, efficient, and environmentally benign method for the acetalization of carbonyl compounds using tetrabutylammonium tribromide (0.01 equiv) as a promoter in the presence of triethyl orthoformate (1.1 equiv) in absolute alcohol at room temperature. Acetals of corresponding carbonyl compounds can also be obtained using trimethyl orthoformate instead of triethyl orthoformate. Open chain acetals have frequently been subjected to special attention, adding to their liability as compared with cyclic *O*,*O*-acetals.[1] Under the experimental conditions, various carbonyl compounds can be acetalized to the corresponding *O*,*O*-acetals in excellent yields, and the result is summarized in Table 1. HBr generated in-situ from the reaction of TBATB with alcohol,[4,7] as shown in Scheme 1, may catalyze the reaction. The solvent also plays a very important role in this reaction. When benzaldehyde (1 equiv) was reacted with triethyl orthoformate (1.1 equiv) and TBATB (0.01

TABLE 1. Acetalization[a] of Carbonyl Compounds (R^1COR^2)

entry	R^1	R^2	time (h)	X_1[b,c]	X_2[b,c]
1	Ph	H	0.16	97	95
2	*p*-(OMe)C_6H_4	H	0.33	80	80
3	*o*-(NO_2)C_6H_4	H	2.50	95	90
4	*p*-(NO_2)C_6H_4	H	0.50	95	92
5	*p*-(Cl)C_6H_4	H	0.16	94	95
6	*o*-(OH)C_6H_4	H	24	00	00
7	*m*-(OH)C_6H_4	H	2.0	62	70
8	*p*-(OH)C_6H_4	H	2.0	25	35
9	4-(OH)-3-(OMe)-C_6H_3	H	0.50	60	60
10	2-(Cl)-6-(NO_2)-C_6H_3	H	3.5	85	60
11	furyl	H	0.16	96	92
12	PhCH=CH	H	0.33	90[d]	93[d]
13	Ph	CH_3	0.33	97	89
14	cyclohexanone		0.33	99	90
15	α-tetralone		0.41	95	87
16	2-cyclopentanone-methyl-carboxylate		2.00	98	89
17	Ph	Ph	24	00	08

[a] Reactions were monitored by TLC/GC. X_1 = dimethyl acetals; X_2 = diethyl acetals. [b] Confirmed by comparison with IR and ^1H NMR of the authentic sample. [c] Isolated yields. [d] Trialkyl orthoformate (2.2 equiv) and 0.02 equiv of TBATB were used.

† Dedicated to professor S. Ranganathan on the occasion of his 68th birthday.

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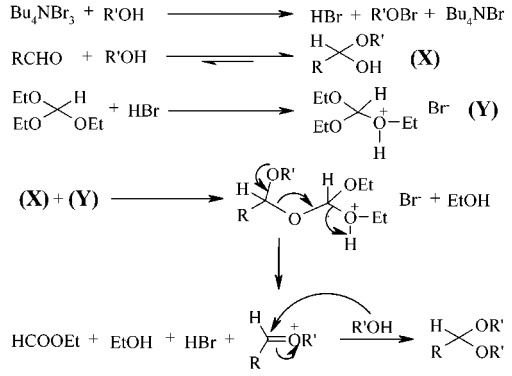
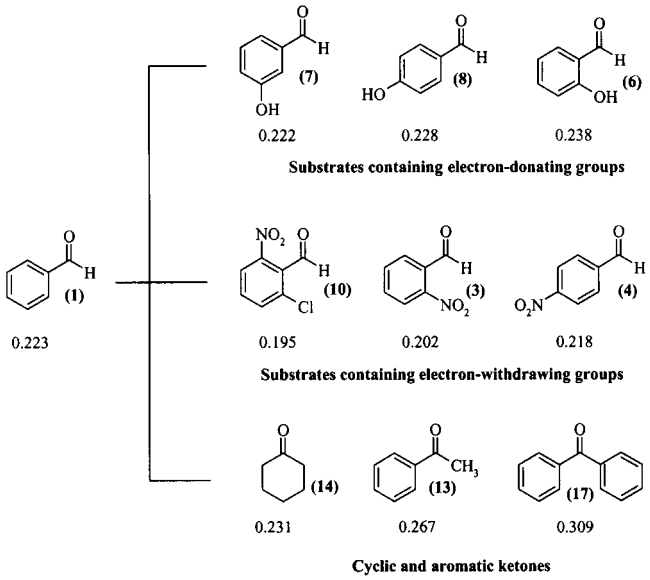
SCHEME 1. Proposed Mechanism of Acetalization



equiv) in CH_2Cl_2, instead of absolute alcohol, after 24 h, only a small amount (<5%) of the corresponding diethyl acetal was formed. This may be due to the fact that alcohol accelerates the formation of a hemiacetal **X**, as shown in Scheme 1, which is further facilitated by the HBr generated in the medium. On the other hand, HBr also protonates triethyl orthoformate to produce an oxonium species **Y**, which in turn reacts with intermediate hemiacetal to give the desired acetal as shown in Scheme 1. In a control experiment, treatment of the reaction mixture with a catalytic amount of a saturated HBr solution in absolute ethanol, instead of TBATB, led to a quantitative conversion of benzaldehyde diethyl acetal within 10 min when benzaldehyde was used as the substrate.

By the present methodology, aromatic aldehyde **1** and substituted aldehydes, with both electron-donating and -withdrawing groups at the ortho and para positions such as **2**−**5**, produced the corresponding dialkyl acetals in excellent yields. It may be mentioned here that the ortho-substituted substrate reacts more slowly than the para-substituted one, which could be due to steric factors. It is interesting to note that the hydroxyl group substituted at different positions in an aromatic ring greatly influences the reaction rates. For instance, the hydroxyl group substituted at the meta and para positions, as in the case of **7** and **8**, in 2 h gave about 70 and 30% of the corresponding dialkyl acetals, respectively. However, when the same group is present at the ortho position (**6**), no product could be detected even after 24 h, which could be due to both steric and electronic factors. It is seen from Table 1 that the electron-donating groups disfavor product formation as demonstrated for **6** and **8**, and the electron-withdrawing group favors the formation of product as shown for **3** and **4**, respectively. In contrast, that electron-withdrawing groups favor the formation of products is further supported with a sterically hindered substrate containing electron-withdrawing groups (**10**). Thus, under the reaction conditions, 2-chloro-6-nitrobenzaldehyde **10** gave dialkyl acetal in 60% yield. To further support our explanation, the electron density at the carbonyl carbon was calculated using semiempirical molecular orbital calculations, the AM1 method as implemented in the Hyperchem package (Hyperchem, Inc.; Gainsville, FL), and the result is shown in Scheme 2. The calculated electron density is in excellent agreement with our explanation. Thus, due to both unfavorable steric and electronic factors, *o*-hydroxybenzaldehyde **6** did not form any trace of dialkyl acetal. For *o*-hydroxybenzaldehyde

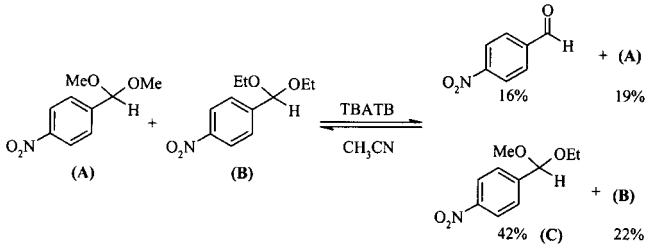
SCHEME 2. Electron Density at the Carbonyl Carbon



6, due to a higher electron density around the carbonyl carbon, it is less susceptible to nucleophilic attack by alcohols. Moreover, a higher activation energy is required due to steric crowding by the *o*-hydroxyl group. For the substrate *p*-hydroxybenzaldehyde **8**, where steric crowding is absent, due to a relatively higher electron density around the carbonyl carbon, it is less susceptible to nucleophilic attack by alcohols for the acetal formation. However, due to a relatively favorable electronic factor and the absence of steric crowding, *m*-hydroxybenzaldehyde **7** gave a better yield than ortho and para hydroxybenzaldehydes. Thus, for acetalization, electronic factors predominate over the steric factors, which is clearly demonstrated in the case of 2-chloro-6-nitrobenzaldehyde **10**. This methodology can also be extended to the heterocyclic aldehyde 2-furaldehyde **11** and unsaturated aldehydes such as cinnamaldehyde **12**.

The formations of dialkyl ketals from the corresponding cyclic and aromatic ketones using conventional acid catalysis were not generally satisfactory due to stereoelectronic factors. It is well-known that aldehydes (RCHO) are more reactive than ketones (RCOR) for two reasons. First, ketones are more stable in the ground state than aldehydes; this is primarily due to the appended alkyl groups providing electron density through the sigma bond framework to stabilize the carbonyl dipole. Second, the transition state for an aldehyde addition reaction is lower in energy than that of the ketone. This is due to steric crowding of the transition state by the ketonic R groups. Since the ketone starts at a lower energy in the ground state, it has a lower reactivity than an aldehyde. However, by the present method, dialkyl ketals were also obtained in high yields when acetophenone **13** and cyclohexanone **14** were used as the models for acyclic and cyclic saturated ketone. The efficacy of the methodology was successfully applied to other ketones such as **15** and **16**. However, the dialkyl ketalization of hindered ketones such as benzophenone **17** was not successful, probably due to the higher electron density at the carbonyl carbon (Scheme 2), thereby making it less susceptible to attack by hydroxyl nucleophiles for ketalization.

SCHEME 3. Transacetalization Reaction



Formation of the mixed acetal was not observed in the above cases since the presence of absolute alcohol was in excess. However, significant amounts of the mixed acetal, ethyl−methyl acetal **C**, could be obtained when alcohol was not used in excess. When benzaldehyde was reacted with triethyl orthoformate (1.1 equiv) in absolute MeOH (0.1 mL, 2.47 equiv), the ratio of dimethyl, ethyl−methyl, and diethyl acetals formed was 70:23:1.3 after 1 h. When the same reaction was performed with trimethyl orthoformate (1.1 equiv) in absolute ethanol (0.1 mL, 1.77 equiv), the product distribution after 1 h was the opposite: the ratio of dimethyl, ethyl−methyl, and diethyl acetals formed was 4:32:60. Unsymmetrical acetals are normally formed from the symmetric diacetals via transacetalization.[8a,b] Treatment of an equimolar mixture of dimethyl acetal **A** and diethyl acetal **B** of *p*-nitrobenzaldehyde with TBATB (0.01 equiv) in acetonitrile after 1 h gave 42% of the unsymmetrical acetal, *p*-nitrobenzaldehyde ethyl−methyl acetal **C**, along with 19% **A**, 22% **B**, and 15% *p*-nitrobenzaldehyde as shown in Scheme 3. Similar acetal exchange has been observed with other acid-catalyzed reactions.[8a,b] The formation of a small amount of *p*-nitrobenzaldehyde could be due to the generation of HBr by the reaction of TBATB with acetonitrile containing a trace amount of water. Thus, our method will be useful for the preparation of unsymmetrical acetals if desired.

Alkoxy exchange also occurs between an acetal and an alcohol through the formation of a mixed acetal. The equilibrium can be shifted to the right by using a large excess of alcohol. Thus, when dimethy acetal **A** (1 equiv) was treated with ethanol (0.1 mL, 1.77 equiv) and TBATB (0.01equiv), significant amounts of ethyl−methyl **C** and diethyl acetals **B** were obtained as shown in Scheme 4.

In another experiment, when diethyl acetal **B** was treated with absolute methanol (0.1 mL, 2.47 eqiuv) in TBATB, dimethyl acetal **A**, along with a small amount of mixed acetal **C**, was obtained as shown in Scheme 4. Thus, mixed acetals and other acetals can be prepared by this methodology using appropriate quantities of alcohol.

Cyclic Acetal Formation. Cyclic acetals such as 1,3-dioxolanes and 1,3-dioxanes are also important protecting groups for carbonyl compounds. They are generally prepared by the reaction of aldehydes and ketones with 1,2-ethanediol or 1,3-propanediol in the presence of acid catalysts[1] under homogeneous conditions. They are also prepared under heterogeneous media using inorganic solids such as $[Zr(O_3PCH_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}]$,[9a] supported silica gel,[9b] Al_2O_3,[9c] clay,[9d,e] zeolites,[9f,g] and kaoline.[9h] Cyclic acetals are generally more easily formed than open chain acetals.[1c] Various aldehydes and ketones gave corresponding 1,3-dioxolanes and 1,3-dioxanes in excellent yields upon treatment with $(EtO)_3CH$ (1.1 equiv), 1,2-ethanediol, or 1,3-propanediol (4 equiv) and a catalytic amount of TBATB (0.01 equiv) as shown in Table 2. Carbonyl compounds such as **1**, **2**, **4**, **6**, and **8** gave the corresponding cyclic acetals in good to excellent yields. It may be mentioned here that acetalization of electron-rich aromatic aldehydes **6** and **8** are generally unsuccessful by conventional methods.[1,2g] Nevertheless, this acetal has been prepared using an expensive ruthenium catalyst and longer reaction times.[10]

SCHEME 4. Acetal Exchange Reaction with an Alcohol

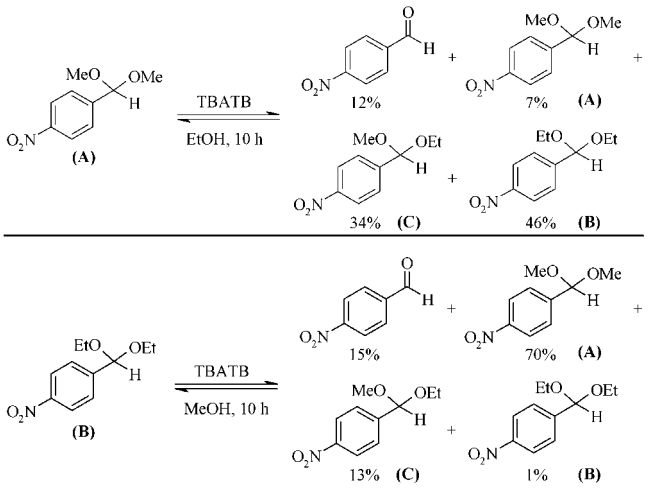


TABLE 2. Acetalization[a] of Carbonyl Compounds (R^1COR^2)

entry	R^1	R^2	time (h)	X_3[b,c]	X_4[b,c]
1	Ph	H	0.08	92	93
2	*p*-(OMe)C_6H_4	H	0.08	75	85
4	*p*-(NO_2)C_6H_4	H	0.5	97	97
6	*o*-(OH)C_6H_4	H	1.5	88[d]	95
8	*p*-(OH)C_6H_4	H	0.08	93[d]	93
10	2-(Cl)-6-(NO_2)-C_6H_3	H	24	00	21
11	furyl	H	0.08	80	85
12	PhCH=CH	H	0.16	65	49
13	Ph	CH_3	0.08	90[d]	80
15	α-tetralone		0.08	94	94
16	2-cyclopentanone-methyl-carboxylate		0.08	97	97
17	Ph	Ph	24	00	64
18	*p*-(OTBDMS)-C_6H_4	H	0.08	92	93

[a] Reactions were monitored by TLC/GC. X_3 = 1,3-dioxolanes; X_4 = 1,3-dioxanes. [b] Confirmed by comparison with IR and ^1H NMR of the authentic sample. [c] Isolated yields. [d] Trialkyl orthoformate (2.2 equiv) and 0.02 equiv of TBATB were used.

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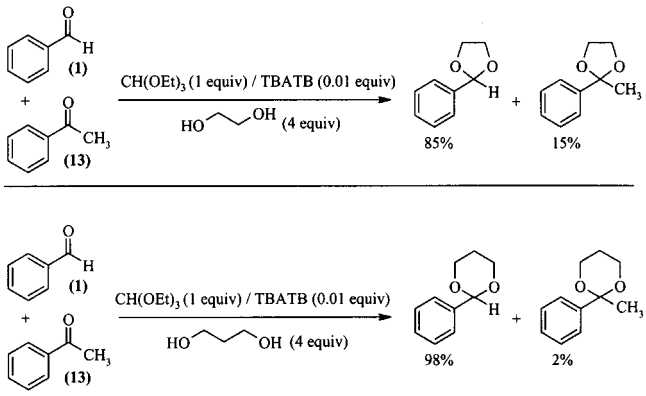
SCHEME 5. Chemoselective Acetalization of Aldehydes



As shown in Table 2, electron-withdrawing groups favored acetal formation as demonstrated with **4**. Sterically hindered aldehyde **10** did not yield any trace of 1,3-dioxolanes but gave a 21% yield of 1,3-dioxanes. This shows the preferential formation of 1,3-dioxanes over 1,3-dioxolanes for the hindered aldehyde. Acid-sensitive substrate **11** and the conjugated carbonyl compound **12** were converted to corresponding cyclic acetals in good yields. Aromatic ketones also formed respective cyclic ketals under these conditions. Substrates **13**, **15**, and **16** could be converted to the corresponding cyclic ketals in satisfactory yields. Hindered ketone **17** gave very a poor yield of 1,3-dioxolanes even after 24 h but gave a moderate yield of 1,3-dioxanes. Thus, from Table 2 it is evident that the unhindered ketone prefers 1,3-dioxolane, while a hindered ketone and an aldehyde prefer 1,3-dioxanes, as demonstrated for substrates **10** and **17**. It is also worthy to note that the aldehyde containing acid-sensitive groups (**18**) such as phenolic OTBDMS gave an excellent yield of cyclic acetals without affecting the phenolic OTBDMS group.

It is well-known that aldehydes react faster than the ketones, which is also the case with our methodology. When an equimolar mixture of benzaldehyde **1** and acetophenone **13** was allowed to react with 1,2-ethanediol, benzaldehyde was chemoselectively acetalyzed over acetophenone. A greater degree of selectivity was found when 1,3-propanediol was used as shown in Scheme 5. Thus, this methodology will be useful for chemoselective acetalization of aldehydes in the presence of ketones.

The preferential formation of 1,3-dioxanes over 1,3-dioxolanes for aldehydes was also supported by the following experiment. When benzaldehyde **1** was reacted in the presence of both 1,2-ethanediol and 1,3-propanediol in equimolar amounts, the ratio of 1,3-dioxolane and 1,3-dioxane was found to be 1:2. It is interesting to note that, when a similar competitive reaction was done with acetophenone **13**, exactly opposite selectivity was observed as shown in Scheme 6, supporting a preferential formation of 1,3-dioxolanes for ketones. From the present study, the apparent order of acetal formation for different carbonyl groups is aldehyde-1,3-dioxanes > aldehyde-1,3-dioxolanes > ketone-1,3-dioxolanes > ketone-1,3-dioxanes.

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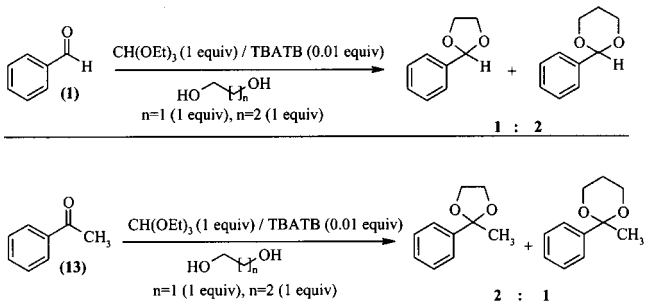
SCHEME 6. Chemoselective Acetalization of Aldehydes



In conclusion, we have shown that acetalization of various carbonyl compounds can be achieved by this methodology. Chemoselective acetalization of aldehydes in the presence of ketones can be accomplished by this method. Cyclic acetals of activated substrates can be achieved in high yields. Acid-sensitive groups such as the phenolic OTBDMS are stable under the reaction conditions. This method is high yielding, safe, operationally simple under mild reaction conditions, and cost effective. The catalytic nature of this methodology makes it more suitable for practical organic synthesis.

Experimental Section

See Supporting Information for details of the instrumentation employed.

Aldehyde containing *tert*-butyldimethylsilyl ether **18** was prepared by silylation of *p*-hydroxybenzaldehyde according to the literature procedures.[14] The following acetals derived from parent aldehydes have been reported in the literature: dimethyl acetals[1c, 11] **1**, **2**, **5**, **12**, and **14**; diethylacetals[2,12] **1**, **2**, **4**, **5**, **12**−**14**, and **17**; 1,3-dioxolanes **1**,[13e] **2**,[2g] **4**,[9a] **6**,[10] **8**,[10] **11**,[13d] **12**,[13e] and **13**;[13e] and 1,3-dioxanes **1**,[2g,13a] **4**,[9a] **6**,[10] **8**,[10] **12**,[2g] and **13**.[2g,13a]

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Supporting Information Available: General procedures for preparation of acyclic and cyclic acetals and chemoselective acetalization of aldehydes in the presence of ketones, and characterization data for the following compounds: dimethyl acetals **3**, **4**, **7**−**11**, **13**, **15**, and **16**; diethylacetals **3**, **7**−**11**, **15**, and **16**; 1,3-dioxolanes **2**, **11**, **15**, **16**, and **18**; and 1,3-dioxanes **2**, **4**, **10**, **11**, and **15**−**18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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