One-Pot Synthesis of Some New α-Bromoketals and Acetals *via* 1,8-Diazabicyclo[5.4.0] Undec-7-ene-Hydrobromide-Perbromide

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ABSTRACT: *α-Bromoketals and acetals are important synthetic precursors in organic synthesis. In this work, some new α-bromoketals are synthesized by the reaction of aryl methyl ketones with diols in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) hydrobromide-perbromide in good isolated yields. The latter compound converts aldehydes to acetals and serves as a new and efficient reagent for the synthesis of acetals. Comparative studies of the preparation of α-bromoketal and acetals using some reported methods versus the present method show that DBUH-Br_3 is one of the most efficient reagents for the preparation of these compounds. Conversion of carbonyl compounds to corresponding α-bromoketals and acetals in the presence of DBUH-Br_3 under microwave irradiation is also described.*

KEYWORDS: *1,8-Diazabicyclo[5.4.0] undec-7-ene (DBU) hydrobromide-perbromide; Aryl methyl ketones; α-Bromoketals; Acetals; Microwave irradiation.*

INTRODUCTION

α-Bromoketals are valuable synthetic precursors in organic synthesis. For example, they are used in preparation of α,β-unsaturated ketones [1-3], and enol-ethers [4]. A study of the vast literature on the one-pot synthesis of α-bromoketals showed that the number of general methods for their preparation from ketones are remarkably few in number. One of the efficient methods for preparation of α-bromoketals is one-pot α-bromoacetalization of carbonyl compound with tribromide [5] and poly (diallyldimethylammonium tribromide) [6] reagents. To overcome the problems of high cost, recovery and recycling of the spent tribromide reagents, we now describe here the one-pot synthesis of new α-bromoketals by 1,8-diazabicyclo[5.4.0] undec-7-ene-hydrobromide-perbromide for the first time.

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1021-9986/2017/3/15-24 10/$/6.00

In the other hand, acetals are used for solvents or intermediates in organic reactions. A thorough compilation of methods for their preparation is given by *Green & Wuts* [7]. Although a lot of conventional catalysts including acid catalysts [7-11] and $Sc(NTf)_3$ [12] have been reported for the conversion of carbonyls into acetals, the search for a new catalyst is still actively pursued due to the problems such as difficulty in handling the reagent, poor chemo-selectivity and limited examples [12]. Here we provide a simple procedure to synthesis of acetals from aldehydes and diols in the presence of DBUH-Br_3.

Furthermore, Microwave irradiation of these reactions provides a fast, efficient and simple method for conversion of carbonyls to α-bromoketals and acetals in excellent isolated yields.

EXPERIMENTAL SECTION

Material and Methods

All chemicals were purchased from Sigma, Fluka or Merck Co (>95% pure). Merck silicagel 60 (230– 400 mesh) was used for flash column chromatography. Solvents were dried by standard methods. All reactions were carried out under an inert atmosphere.

Equipment

Melting points were measured on an Electrothermal type-9100 melting- point apparatus. The IR spectra (as KBr discs) were obtained on a Tensor 27 spectrometer. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DRX- 400 Fourier-transformer spectrometer with TMS used as an internal standard. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyser. Reactions were conducted in a Micro SYNTH. All reagents were commercially available from Merck and Aldrich.

Preparation of the DBUH$^+$Br$_3^-$ complex [13,14]

A solution of bromine (28 mmol, 10.0 g) in dry chloroform (50 cm^3) was added drop-wise with stirring to a solution of DBU (14 mmol, 4.5 g) in dry chloroform (50 cm^3) at 0–5°C. As the bromine was added, an orange solid appeared. The mixture was stirred for an additional 2 h, and then the residue was collected by filtration and washed with chloroform (20 cm^3). (Yield = 12 g (87%), m.p. = 123–124°C). *DBUH-Br_3:* ^1H NMR (400 MHz, $CDCl_3$) δ 1.8–3.7 (m, 16H), 8.4

(s, 1H, NH, D_2O exchangeable). FT-IR (KBr disc) 3384.4 cm^{-1} (N-H), 1584 cm^{-1} (C=N).

Conversion of aryl methyl ketones to α-bromoketals with DBUH-Br_3; general procedure

A mixture of the aryl methyl ketone (1 mmol), the diols (3 mmol) and triethyl orthoformate (0.44g, 3 mmol) in dry dichloromethane (5 cm^3) was stirred under reflux in the presence of DBUH-Br_3 (0.47 g, 1 mmol) for an appropriate time (Table 2). After completion of the reaction, as monitored by TLC, $NaHCO_3$ 5% (5 cm^3) was added and the organic layers was washed with water (2×5 cm^3). The combined organic layers were dried over anhydrous $MgSO_4$. After evaporation of the solvent, practically pure product was obtained. For further purification, the product was purified by flash column chromatography (n-hexane/ethyl acetate, 10:1).

The general procedure for the acetalization of aldehydes in the presence of DBUH-Br_3.

To a mixture of various aromatic aldehydes (1 mmol), triethyl orthoformate (0.44g, 3 mmol) and diols (3 mmol) in dry dichloromethane (5 cm^3), DBUH-Br_3 (0.94 g, 2 mmol) was added. Then the mixture was refluxed for an appropriate time (Table 4) and the progress of the reaction was monitored by TLC. After completion of the reaction, $NaHCO_3$ 5% (5 cm^3) was added and the organic layers was washed with water (2×5 cm^3). The combined organic layers were dried over anhydrous $MgSO_4$. After evaporation of the solvent, practically pure product was obtained. For further purification, the product was purified by flash column chromatography (n-hexane/ethyl acetate, 10:1).

The general procedure for α-bromoketalization and acetalization of aryl methyl ketones and aldehydes in the presence of DBUH-Br_3 mediated by Microwave Irradiation.

A mixture of the aryl methyl ketone or aromatic aldehydes (1 mmol) and triethyl orthoformate (0.44g, 3 mmol) were treated with diols (3 mmol) in the presence of DBU-hydrobromide-perbromide (0.94 g, 2 mmol) in dry acetonitrile (3 cm^3) under microwave irradiation for an appropriate time (Table 5). The work-up procedure is the same as mentioned above.

2-(Bromomethyl)-2-phenyl-1,3-dioxolane (3a)

m.p.: 57-58 °C (lit.[15] m.p.: 58-59) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.67 (s, 2H) , 3.85-3.95 (m, 2H), 4.24-4.44 (m, 2H), 7.33-7.40 (m, 3H), 7.49-7.57 (m, 2H) ppm; ^{13}C NMR (100 MHz , $CDCl_3$): δ 38.0, 66.0, 107.4, 126.1, 128.5, 139.8. IR (ν, cm^{-1}): 3066 (C-H), 3033, 2939, 1600, 1495, 1374, 1276, 1178, 1112 (C-O), 895, 716, 620 (C-Br).

2-(Bromomethyl)-5,5-dimethyl-2-phenyl-1,3-dioxane (3b)

m.p.: 67-70 °C (lit.[16] mp: 66-68). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.62 (s, 3H), 1.38 (s, 3H), 3.48(s, 2H), 3.51(q, 4H), 7.30-7.50 (m, 5H). IR (ν, cm^{-1}): 3026 (C-H), 2985, 2960, 1077 (C-O), 616 (C-Br). m/z 284 (M^+), 286 $(M+2)^+$. Anal.Calcd for $C_{13}H_{17}BrO_2$; C, 54.75; H, 6.01; Found C, 54.66; H, 5. 92%.

2-(Bromomethyl)-2(4-bromophenyl)-1,3-dioxolane (3c)

m.p.: 79-80 °C (lit.[15] mp: 80-81 °C) ^{1}H NMR($CDCl_3$, 400 MHz): δ 3.61 (s, 2H), 3.83-3.94 (m, 2H), 4.13-4.23 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 2H),7.49 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9, 66.0, 107.1, 123.2, 128.0, 131.6, 138.9. IR (ν, cm^{-1}): 3084, 3060, 2990, 2957, 2928, 1691, 1575, 1373, 1249, 1144, 1040, 947, 826.

2-(Bromomethyl)-2-(4-bromophenyl)-5,5-dimethyl-1,3-dioxane (3d)

m.p.: 104-106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.63 (s, 3H), 1.37(s, 3H), 3.45 (s, 2H), 3.47 (q, *J* = 10.8 Hz, 4H), 7.36 (d ,2H, *J*= 8.4 Hz), 7.58 (d, 2H, *J* = 8.4 Hz). IR (ν, cm^{-1}): 3027 (C-H), 2959, 2908, 1074 (C-O), 626(C-Br). m/z: 361$(M)^+$, 365 $(M+4)^+$. Anal.Calcd for $C_{13}H_{16}Br_2O_2$; C, 42.89; H, 4.43; Found C, 42.77; H, 4.39%.

2-(Bromomethyl)-2-(3,4-dimethoxyphenyl)-5,5-dimethyl-1,3-dioxan (3e)

m.p.:106-108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.63 (s, 3H), 1.39 (s, 3H), 3.49-3.54 (m, 6H), 3.91 (s, 3H), 3.93 (s, 3H), 6.93 (d, 1H, *J* = 8.4 Hz), 6.98 (d, 1H, *J* = 2.0 Hz), 7.05 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz). IR (ν, cm^{-1}): 3008 (C-H), 2955, 2932, 1027 (C-O), 687 (C-Br). m/z: 344 $(M)^+$, 346 $(M+2)^+$. Anal.Calcd for $C_{15}H_{21}BrO_4$; C, 52.19; H, 6.13; Found C, 52.45; H, 6.17%.

2-(Biphenyl-4-yl)-2-(bromomethyl)-5,5-dimethyl-1,3-dioxane (3f)

m.p.:96-98 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.65 (s, 3H), 1.43 (s, 3H), 3.53-3.60 (m, 6H), 7.41 (t, 1H, *J* = 7.6 Hz), 7.49 (t, 2H, *J* = 7.6 Hz), 7.56 (d, 2H, *J*=8.4 Hz), 7.67 (dd, 4H, J_1= 8.4 Hz, J_2 = 7.2 Hz). IR (ν, cm^{-1}): 2963, 2928, 1077 (C-O), 689 (C-Br). m/z: 361 $(M)^+$, 363 $(M+2)^+$. Anal.Calcd for $C_{19}H_{21}BrO_2$; C, 63.17; H, 5.86; Found C, 63.53; H, 5. 95%.

2-Phenyl-1,3-dioxolane (3g)

Liquid (lit.[17] liquid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.85 (s, 4H), 6.18 (s, 1H), 7.21-7.29 (m, 5H). IR (ν, cm^{-1}): 3066, 3036, 2954, 1494, 1460, 1396, 1312, 1294, 1221, 1168, 1094, 1071, 1028, 944, 916, 759. ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.2, 109.1, 127.6, 128.4, 129.6, 137.3.

2-(2-Chlorophenyl)-1,3-dioxolane (3h)

Liquid (lit.[18] liquid). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.04-4.11 (m, 4H), 6.16 (s, 1H), 7.34-7.41 (m, 4H). IR (ν, cm^{-1}): 3071, 2956, 1594 (HC=C), 1095(C-O), 1049, 943. ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.4, 100.7, 100.7, 126.8, 127.5, 129.7, 130.3, 135.0.

2-(4-Chlorophenyl)-1,3-dioxolane (3i)

Liquid (lit.[18] liquid) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.08-4.15 (m, 4H), 5.77 (s, 1H), 7.34 (d, 2H, *J* = 8.5 Hz), 7.37 (2d, 2H, *J* = 8.5 Hz); ^{13}C NMR (100 MHz , $CDCl_3$): δ 65.2, 102.9, 127.8, 128.5, 130.8, 136.4. IR (ν, cm^{-1}): 3057, 2955, 1599 (HC=C), 1089 (C-O), 1015, 819.

2-(2-Methoxyphenyl) -5,5-dimethyl-1,3-dioxane (3j)

Liquid (lit.[16] liquid) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.85(s, 3H), 1.32 (s, 3H), 3.62 (q, 4H), 3.77 (s, 3H), 5.33 (s, 1H), 7.23-7.30 (m, 4H). IR (ν, cm^{-1}): 3007, 2979, 1125. m/z: 222 (M^+). Anal.Calcd for $C_{13}H_{18}O_3$; C, 70.24; H, 8.16; Found C, 70.18; H, 8, 16%.

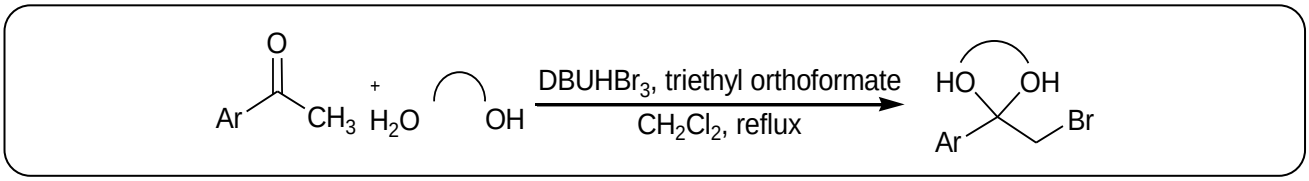
2-(4-Nitrophenyl)-5,5-dimethyl -1,3-dioxane (3k)

m.p.: 46-48 °C (lit.[19] m.p.: 48 °C) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80 (s, 3H), 1.27 (s, 3H), 3.71 (s, 4H), 5.39 (s, 1H),7.50-7.56 (m, 4H). IR (ν, cm^{-1}): 2981, 2960, 2858, 1530 (N=O), 1350 (N=O), 1100 (C-O).

Table 1: Determining the best reaction conditions in treatment of acetophenone with ethane-1,2-diol in the presence of DBUH-Br$_3$ under different solvents and temperatures.

Entry	Solvent	Temperature	Time/min	Yield[a]/%
1	DMF	rt	150	30
2	DMF	reflux	70	45
3	CH_2Cl_2	rt	120	55
4	CH_2Cl_2	reflux	30	83
5	CH_3CN	rt	120	35
6	CH_3CN	reflux	120	46

[a] *Isolated yields*



Scheme 1. α-Bromoketalization of a series of aryl methyl ketones with diols and DBUHBr$_3$

2-(4-Bromophenyl)-1,3-dioxolane (3l)

m.p.: 36-38 °C (lit.[20] mp: 37-38 °C) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.00-4.03 (m, 2H), 4.07-4.10 (m, 2H), 5.76 (s, 1H), 7.34 (d, 2H, *J* = 8.2 Hz), 7.50 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.1, 103.6, 124.3, 129.9, 132.5, 137.7. IR (ν, cm^{-1}): 2886 (C-H), 1595 (Ar-H), 1082 (C-O).

RESULTS AND DISCUSSION

Synthesis of α-bromoketals

The synthesis and X-ray structure of DBUH-Br$_3$ have been reported elsewhere [13]. The influence of different amounts of DBUH-Br$_3$, different solvents, temperature, and reaction time on the isolated yield of product was investigated in the reaction of 1 mmol acetophenone with 3 mmol ethane-1,2-diol in the presence of 1 mmol DBU-hydrobromideperbromide. As depicted in Table 1, the best result was obtained in dichloromethane as a solvent under reflux conditions (entry 4).

To study the scope of this protocol, the α-bromoketalization of a series of aryl methyl ketones with diols was carried out (Scheme 1). The results are summarized in Table 2.

Other ketones such as cyclohexanone, benzophenone and aliphatic ketones diminish the effectiveness of the reaction. The products **3d-f** are new derivatives of α-bromoketals and are synthesized from the reaction of neopentyl glycol (**2b**) with 4-bromoacetophenone, 3,4-dimethoxyacetophenone and 4-phenylacetophenone respectively. The structural assignments of compounds **3a-f** were based on the analytical and spectral data (Experimental Section).

A tentative mechanism for this reaction is proposed in Scheme 2.

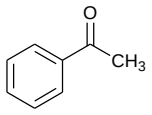
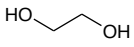
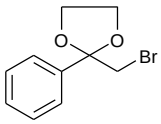
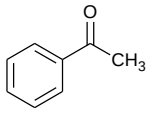
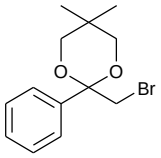
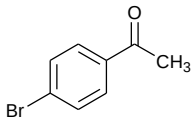
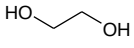
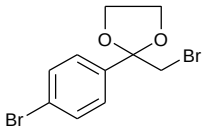
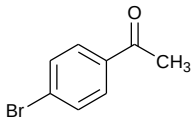
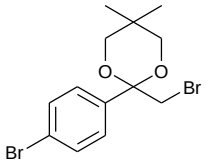
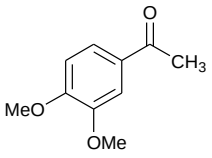
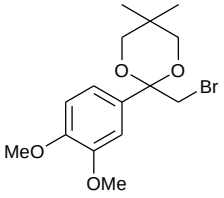
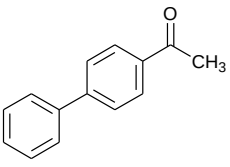
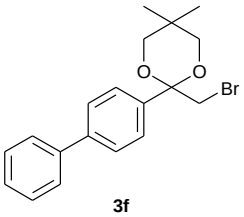
In order to evaluate the capability of the present method with respect to the reported methods for the preparation of α-bromoketal, the synthesis of compound **3a** was compared with the reported methods (Table 3). As it is clear from Table 3, the present method is more efficient.

Synthesis of acetals

For determining the best reaction conditions, we studied the reaction of 1 mmol benzaldehyde with 3 mmol ethane-1,2-diol in the presence of 1mmol DBU-hydrobromideperbromide under different conditions. As shown in Table 4, the best result was obtained in dichloromethane as a solvent under reflux conditions (entry 4).

With the optimized reaction conditions in hand, we examined the scope of the DBU-hydrobromide-perbromide system for the synthesis of acetals (Scheme 3). In general, the DBU-hydrobromide-perbromide catalysed acetalization occurs smoothly to provide the desired products in good isolated yields (Table 5).

Table 2: α-Bromoketalization of a series of aryl methyl ketones with diols in the presence of DBUH-Br3 in dichloromethane.

Entry	Aryl methyl ketones	Diols	Time(min)	Product	Yield[a](%)	M.p °C/Lit.[b]
1	 **1a**	 **2a**	30	 **3a**	83	57-58 (lit.[15] m.p.: 58-59)
2	 **1a**	 **2b**	40	 **3b**	80	67-70 (lit.[16] mp: 66-68)
3	 **1b**	 **2a**	25	 **3c**	86	79-80 (lit.[15] mp: 80-81)
4	 **1b**	 **2b**	35	 **3d**	82	104-106
5	 **1c**	 **2b**	45	 **3e**	65	106-108
6	 **1d**	 **2b**	60	 **3f**	80	96-98

a) Isolated yields

b) The products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by the procedure given in the references.

Table 3: Comparative the preparation of α-bromoketal using the reported methods versus the present method.

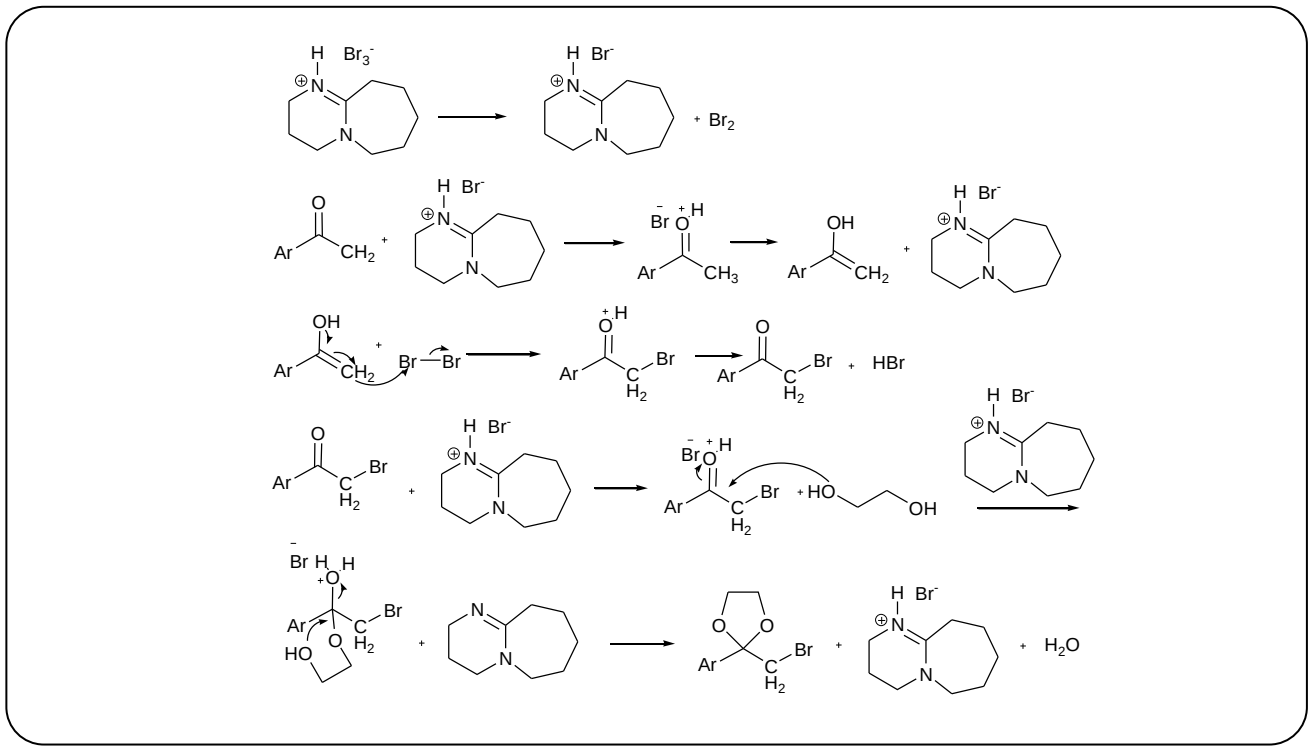
Entry	Reagent and Conditions	Time/h	Yield[a]/%	Ref.
1	acetophenone, ethane-1,2-diol, DBUH-Br_3, reflux	0.5	83	-
2	Styrene, NaBr, $HOCH_2CH_2OH$, electrolysis, 60 °C	1	60	6
3	acetophenone, ethane-1,2-diol, poly(diallyldimethylammonium tribromide), reflux	20	82	21
4	acetophenone, ethane-1,2-diol, pyridinium perbromide, reflux	2	80	22
5	phenacyl bromide, spiroorthocarbonate, rt	1	80	24

[a] *Isolated yields*

Table 4: Selected conditions screened for the reaction of benzaldehyde with ethane-1,2-diol.

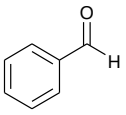
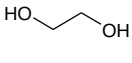
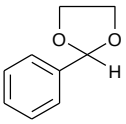
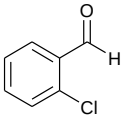
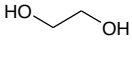
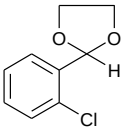
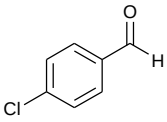
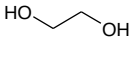
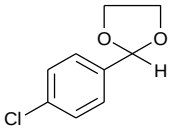
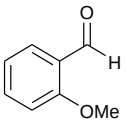
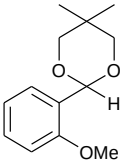
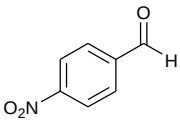
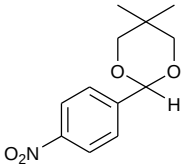
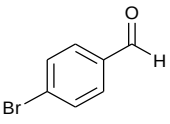
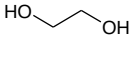
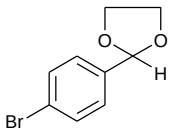
Entry	Solvent	Temperature	Time/min	Yield[a]/%
1	DMF	rt	60	45
2	DMF	reflux	60	55
3	CH_2Cl_2	rt	60	85
4	CH_2Cl_2	reflux	20	90
5	CH_3CN	rt	120	56
6	CH_3CN	reflux	90	63

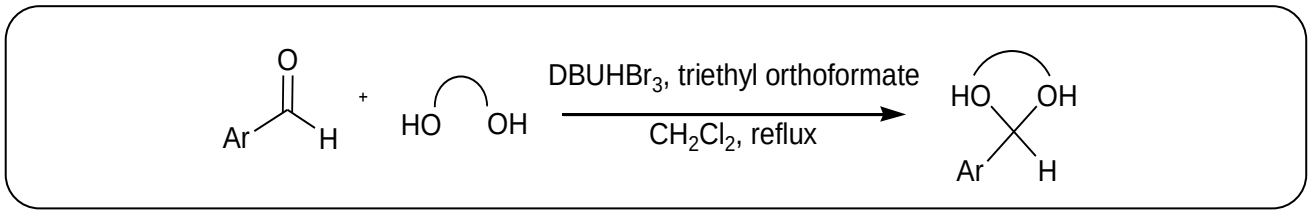
[a] *Isolated yields*



Scheme 2: A proposed reaction mechanism for the synthesis of α-bromoketals with DBUH-Br3.

Table 5: Acetalization of aromatic aldehydes with diols in the presence of DBUH-Br3 in dichloromethane as a solvent under reflux conditions.

Entry	Substrate	Diols	Time (min)	Product	Yield[a] (%)	M.p °C/Lit.[b]
1	 **1e**	 **2a**	20	 **3g**	90	Liquid (lit.[17] liquid)
2	 **1f**	 **2a**	10	 **3h**	95	Liquid (lit.[18] liquid)
3	 **1g**	 **2a**	10	 **3i**	93	Liquid (lit.[18] liquid)
4	 **1h**	 **2b**	15	 **3j**	80	Liquid (lit.[16] liquid)
5	 **1i**	 **2b**	15	 **3k**	93	46-48 (lit.[19] m.p.: 48)
6	 **1j**	 **2a**	18	 **3l**	90	36-38 ° (lit.[20] mp: 37-38)



Scheme 3: Acetalization of aromatic aldehydes with diols in the presence of DBUH-Br3.

Table 6: Acetalization of benzaldehyde with ethane-1,2-diol using some reported methods compared the present method.

Entry	Reagent and Conditions	Time/min	Yield[a]/%	Ref.
1	DBUH-Br_3, reflux	20	90	-
2	hydroxy complexes of palladium(II), rt	180	72	23
3	I_2, rt	960	70	24
4	bis(perfluorooctanesulfonyl)imide, reflux	120	97	25
5	*para*-toluene sulfonic acid, MW	30	78	8
6	Ce^{3+}-Mont, rt	720	97	9
7	silica-bound sulfuric acid, reflux	1	58	26
8	Tetrabutylammonium Tribromide, rt	16	90	27
9	Benzyltriphenylphosphonium tribromide, rt	23	90	28
10	Benzyltriphenylphosphonium tribromide, rt	25	89	29

[a] *Isolated yields*

Table 7: α-Bromoketalization and acetalization reactions in the presence of DBUH-Br3 under microwave irradiation.

Entry	Carbonyl compounds	Diols	Product	Power (W)	Time (min)	Yield[a] (%)
1	Acetophenone	2a	3a	400	2	90
2	Acetophenone	2b	3b	400	4	89
3	4-Bromoacetophenone	2a	3c	400	2	93
4	4-Bromoacetophenone	2b	3d	400	3	92
5	3,4-Dimethoxyacetophenone	2b	3e	400	5	88
6	4-Phenylacetophenone	2b	3f	400	7	85
7	Benzaldehyde	2a	3g	300	2	95
8	2-Chlorobenzaldehyde	2a	3h	300	1	98
9	4-Chlorobenzaldehyde	2a	3i	300	1	95
10	2-Methoxybenzaldehyde	2b	3j	300	2	94
11	4-Nitrobenzaldehyde	2b	3k	300	2	95
12	4-Bromobenzaldehyde	2a	3l	300	1	96

The acetalization reaction was amenable to both electron-rich and electron-poor aromatic aldehydes (entry 4 and 5). The structural assignments of compounds **3g-l** were based on the analytical and spectral data.

To compare the efficiency of the method with the previous methods, acetalization of benzaldehyde with ethane-1,2-diol in the presence of DBUH-Br_3 was contrasted with some reported methods. As it is obvious from Table 6, the current method is one of the most efficient methods.

α-Bromoketalization and acetalization under microwave irradiation

Carbonyl compounds were treated with 3 equivalents of diols in the presence of DBU-hydrobromide-perbromide under microwave irradiation leading to α-bromoketals and acetals in satisfactory isolated yields. Acetonitrile was used as solvent because of its high dielectric constant and outstanding solubility. As is demonstrated in Table 7, in all cases our protocol gave shorter reaction time and higher yields than presented method in this work.

CONCLUSIONS

In current work, we have developed α-bromoketalization and acetalization reactions catalysed by DBU-hydrobromide-perbromide and microwave irradiation promotes the yields of these reactions. Further investigation into the scope and synthetic application of DBUH-Br_3 are in progress and will be reported elsewhere.

Received : Apr. 12, 2016 ; Accepted : Oct. 17, 2016

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