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Investigating the effectiveness of classical and eco-friendly approaches for synthesis of dialdehydes from organic dihalides

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Abstract: Monoaldehydes and dialdehydes are parts of millions of compounds and are extremely versatile intermediates. For the synthesis of monoaldehydes, one impressive approach to date, because of its excellent selectivity, high yield and stability towards over-oxidation and over-reduction, is the oxidation of organic monohalides. Numerous monohalides oxidation based methodologies to afford monoaldehydes are disclosed in literature. In this research work, twelve well-known approaches (well-documented for synthesis of monoaldehydes from monohalides) are investigated for their effectiveness towards synthesis of organic dialdehydes from organic dihalides. The classical approaches under investigation include modified Sommelet oxidation, Kröhnke oxidation, sodium periodate-mediated oxidative protocol, manganese dioxide-based oxidative approach, Kornblum oxidation and Hass-Bender oxidation. The eco-friendly approaches under observation include periodic acid-based IL protocol, periodic acid in vanadium pentoxide-mediated IL method, hydrogen peroxide in vanadium pentoxide-based approach, hydrogen peroxide-mediated IL methodology, IBX-assisted IL protocol and bismuth nitrate-promoted IL technique. In this investigation yield, overoxidation, eco-friendliness, cost-effectiveness and recyclability are the main parameters which are under examination. Hopefully, this research will help chemists in carrying out routine operations in organic synthesis and will also be fruitful to select finest synthetic approach, develop further new transformational methodologies and improve current transformational approaches for the synthesis of dialdehydes.

Keywords: aldehydes; ketones; oxidation; green synthesis; ionic liquid

1 Introduction

Dialdehyde containing organic compounds are well-known and important entities. These entities are significant categories of chemicals that have been widely employed as precursors and starting materials in the production of series of fine and special chemicals such as polymers, vitamins, drugs, nanomaterials, fragrances, photochromic materials, organic conductors, agrochemicals, sensors, and dyes etc. [1,2]. Moreover, in organic chemistry symmetrical dialdehydes are important precursors and are widely employed for the synthesis of important symmetrical compounds, for example, in the synthesis of spiro-OMeTAD (hole transport materials in DSSC solar cells), formation of plastic crystals, quinoxaline analogues preparation (good chromophores for applications in photoluminescence), synthesis of tetraoxacirculenes (organic light-emitting diodes), preparation of *o*-substituted dioximes of benzo-fused *β*-diketocyclo-alkylenes (precursors for synthesis of drugs), formation of HIV protease inhibitors and synthesis of symmetrical dye derivatives etc. [3,4]. Furthermore, dialdehydes are widespread in nature and are part of millions of chemicals, for instance, many dialdehyde units are components of essential oils and give these oils auspicious odors [5].

Dialdehydes are predominantly advantageous as functional groups due to their wide range of additional conversions that are achievable. They can possibly act as electrophiles and besides, by elimination of an alpha-proton, they can also bring about nucleophilic reactions. These types of potential chemical reactions cause dialdehydes to act potentially and extremely useful precursors for many reactions [6]. Generally, there

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are two pathways which are used for the synthesis of dialdehydes, that is, (i) direct methods: these methods are predominantly applicable for the preparation of aromatic dialdehydes [7]. These methods comprise direct introduction of the carbonyl entity, or groups that can be transformed into carbonyl group or into the aromatic nucleus directly, and (ii) indirect methods: the term means to describe the conversion of groups already present on the aromatic nucleus into the aldehyde groups.

In choosing any one of the above methods to furnish an aromatic aldehyde it is essential to consider the effect of groups already in the core, since this influence orientation, activation or deactivation of the ring and side reactions with the reagents [7-9]. In the field of organic synthesis direct methods are less valuable then indirect methods due to the dependence of direct methods on ring substituent effects [9].

Amongst all the indirect methods, the transformation of organic dihalides into dialdehydes is highly suitable procedure. The high suitability of this transformational approach is due to three reasons: (i) usually it prevents over-oxidation and over-reduction which are very frequent in indirect methods, for example, in the process of conversion of organic dialcohols to dialdehydes over-oxidation is a common phenomenon whereas in the production of dialdehydes from the transformation of organic diacids or diesters over-reduction occurs very frequently, (ii) generally organic dihalides-mediated conversion offers high selectivity and (iii) in the majority of cases outstanding yield is attained [10,11]. Hence, oxidation of organic dihalides is the most promising methodology to construct dialdehyde frameworks. However, by using any method (direct or indirect approach), the synthesis of dialdehyde is difficult as compared to monoaldehyde synthesis [12]. By using dihalide-oxidative approach, following are the observed difficulties in few cases: (i) some classical methods lead towards formation of acidic products due to over-oxidation and (ii) some approaches result in formation of more than one product (mono- and di-products).

Unfortunately in literature, most organic halide-based transformational techniques are concerned with the synthesis of monoaldehyde and good research has been less targeted in the field of synthesis of dialdehydes from organic dihalides [12]. To fill this research gap and find out the most promising approach, herein, synthetic methods are investigated at wide level. In this research work, all the well-known oxidative protocols which have been reported for the synthesis of monoaldehydes from organic monohalides, are assessed for their effectiveness towards the synthesis of dialdehydes from organic dihalides.

2 Experimental

2.1 Materials and general methods

In this research work, except **1**, **12** and **19**, all reagents and other chemicals were obtained from Fluka, Merck and Sigma-Aldrich. The precursor **1** was prepared by the two-step reported method of Mancilha et al. [13] and Page et al. [14], precursor **12** was prepared according to the reported method of Asakawa et al. [15] and precursor **19** was obtained through the procedure of Pesin et al. [16]. All reagents and other chemicals were used without additional purification, while all the solvents were purified through distillation before use. Proton and carbon nuclear magnetic resonance spectra were measured at 300 MHz on a Varian Gem2300 300 MHz spectrometer. Tetramethylsilane (TMS) as an internal standard and dimethyl sulfoxide (DMSO) as solvent were used. Chemical shifts were expressed in ppm units. All melting points were determined on a Mel-Temp melting point device. The reaction progress was monitored through pre-coated silica gel-60 TLC plates. The compound **13** is unreported, while compounds **1**, **2**, **9**, **11**, **15**, **18**, **21**, **23**, **25**, **27** and **29**. The structural characterizations are given except for those compounds which are commercially available.

2.2 General procedure of modified Sommelet reaction for synthesis of dialdehydes

Hexamethylenetetramine **1** (1 mmol), sodium dodecyl sulfate (0.22 mmol) and lanthanum triflate (0.06 mmol) were dissolved in water (1 mL). Then organic dihalide (1.26 mmol) was added to the flask. The mixture was refluxed until the reaction was completed, which was observed via TLC in the solvent system of 10% EtOAc in hexane. The mixture was extracted three times with ethyl acetate and the combined organic phases were evaporated under *vacuo*. The crude mixture was decontaminated via silica gel based chromatographic purification technique, in which ethyl acetate in hexane (1:2) as eluent was employed to afford the desired product.

2.3 General procedure of Kröhnke reaction for synthesis of dialdehydes

2.3.1 Preparation of bis(pyridinium ylide)

Organic dihalide was heated with excess pyridine at 100°C until the reaction was completed (monitored via TLC in the solvent system of 10% EtOAc in hexane) to afford bis(pyridinium ylide).

2.3.2 Preparation of the bis(nitrone)

A suspension of 0.02 mol of bis(pyridinium ylide) and 2 g of sodium amide in 40 mL pyridine was prepared. Then, 0.04 mol of highly purified *N*,*N*-dimethyl-4-nitrosoaniline and 10 mL of water were added very slowly at 20 to 30°C with stirring, to start the reaction. After completion of reaction (usually within 12 h; monitored by TLC in the solvent system of 10% EtOAc in hexane), the mixture was cooled in ice and filtered and then recrystallized in dimethylformamide to furnish bis(nitrone).

2.3.3 Preparation of dialdehyde

The bis(nitrone) (0.04 mol) was decomposed in a separation funnel with 300-400 mL of 2 M HCI under (means) 300 mL of ether. The mixture was shaken for about 15-25 min and extracted four times with 100 mL portions of Et_2O; the extracts of ether were then combined, washed three times with freshly distilled H_2O, and dehydrated with assistance of sulfate of soda. After evaporating solvent under *vacuo*, the crude mixture was decontaminated via silica gel-based chromatographic purification technique, in which ethyl acetate in hexane (1:2) as eluent was employed to afford desired product.

2.4 General procedure of Sasmita protocol for synthesis of dialdehydes

In a round bottom flask of 250 mL, organic dihalide (20 mmol) was taken along with $NaIO_4$ (8 mmol). Then, in this mixture, 90 mL of DMF was added. The reaction mixture was heated at 150°C. After accomplishment of oxidation reaction (observed by TLC in the solvent system of 10% ethyl acetate-hexane), the mixture was cooled to room temperature, treated with H_2O (60 mL) and then extracted several times with Et_2O. After drying the combined layers of ether extract via $MgSO_4$, chromatographic purification was performed in which ethyl acetate in hexane (1:2) as eluent was employed to afford desired product.

2.5 General procedure of manganese dioxide-based oxidation for synthesis of dialdehydes

2.5.1 Preparation of activated manganese dioxide

On a large Buchner funnel, MnO_2 (25 g) was placed and then 15% spirit of niter (40 mL) was poured gradually. After washing with spirit of niter was finished, the MnO_2 cake was treated with one liter of freshly distilled H_2O or until the filtrate become neutral. MnO_2 was dried at temperature of 105°C, for 48 h and then could be kept under ordinary conditions of laboratory for several weeks without activity loss [17].

2.5.2 General procedure for synthesis of dialdehydes

A mixture of organic dihalide (2 mmol) and activated manganese dioxide (20 mmol) in chloroform (40 mL) was refluxed until the oxidative reaction was finalized, which was observed by TLC in the solvent system of 10% ethyl acetate in n-hexane. After accomplishment of reaction, the mixture was filtered and treated with trichloromethane. The combined filtrates after distillation and silica gel (ethyl acetate/hexanes: 1:2) purification afforded desired product [18].

2.6 General procedure of Kornblum reaction for synthesis of dialdehydes

In first step, a mixture of DMSO (400 mL) and $NaHCO_3$ (668 mmol) was carefully degassed. Then, under N_2 gas, this mixture was heated at temperature of 150°C. Next, in one portion, organic dihalide (64 mmol) was added to mixture and after that, it was vigorously stirred at temperature of 150°C for appropriate time (controlled through TLC in the solvent system of 10% EtOAc in hexane) before it was cooled to room temperature over 20 min. Et_2O (300 mL) was poured in mixture, and subsequently H_2O (300 mL) was poured. The layers were isolated and the aqueous layer was extracted several times with Et_2O. The layers of combined organic extracts were treated with H_2O, dried through magnesium sulfate and evaporated under *vacuo*. The crude mixture was decontaminated via silica gel-based chromatographic purification technique, in which ethyl acetate in hexanes (1:2) as eluent was employed to afford desired product.

2.7 General procedure of Hass-Bender reaction for synthesis of dialdehydes

A mixture of 2-nitropropane (4.96 mmol) and sodium methoxide (6.68 mmol) in 20 mL of MeOH was heated under reflux for appropriate time (controlled through TLC in the solvent system of 10% EtOAc in hexane) and then cooled to room temperature. Organic dihalide (1.78 mmol) was added and the mixture was vigorously stirred at r.t for 2 h. After MeOH removal under *vacuo* by rotary evaporator, the remainder was partitioned between dichloromethane (400 mL) and water (100 mL). The layer of organic solvent was dried via magnesium sulfate and concentrated under *vacuo*. The crude product was chromatographically purified through ethyl acetate in hexane (1:2) as eluent to get desired product.

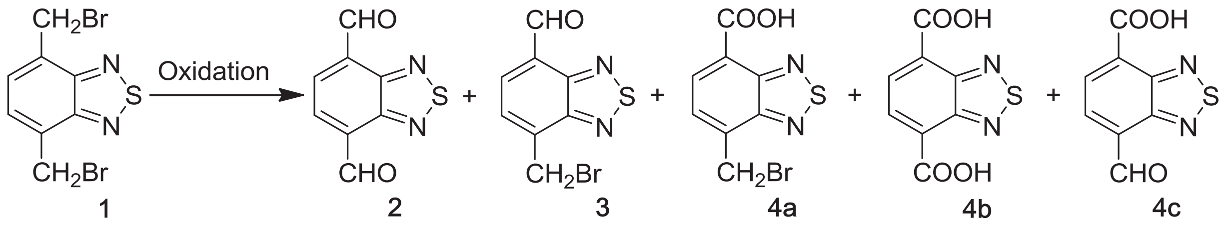
2.8 General procedure of Ming protocol A for synthesis of dialdehydes

To a vigorously stirred solution of organic dihalide (20 mmol) in [C_{12}mim][$FeCl_4$] (1.6 mmol), H_5IO_6 (44 mmol) was introduced. Then, under vigorously stirring for an appropriate period of time and temperature (Tables 1 and 3), the progress of reaction was observed by TLC in the solvent system of 10% EtOAc in hexane. Upon reaction completion, the mixture was extracted three times with DCM (3 × 10 mL). The solution of DCM was treated with 10% $NaHCO_3$ and dried through anhydrous sulfate of soda. The liquid products were decontaminated via distillation, whereas solid product were decontaminated via recrystallization from EtOAc and *n*-hexane. Under similar conditions, the recovered catalytic system was then reused.

2.9 General procedure of Ming protocol B for synthesis of dialdehydes

To a vigorously stirred mixture of organic dihalide (20 mmol) in IL [bmpy]PF_6 (20 mL), H_5IO_6 (48 mmol) and V_2O_5 (1.4 mmol) were added at r.t and vigorously stirring was continued for an appropriate period of time and temperature (Tables 1 and 3). After reaction completion, as showed by TLC (solvent system of 10% EtOAc in hexane), the product was extracted with dichloromethane

Table 1: Application of different oxidative protocols for synthesis of dialdehydes from organic dihalides.



Entry	Name of reaction approach	Reaction conditions	Yield of 2*	Yield of 3*	Acidic products (4a, 4b and 4c)*
1	Modified Sommelet oxidation	Urotropin, sodium dodecyl sulfate, La(OTf)$_2$ (cat.), H_2O, reflux for 6 h	65%	12%	Traces
2	Kröhnke oxidation	i) Py ii) *N*,*N*-dimethyl-4-nitrosoaniline iii) H_3O^+	50%	18%	>10%
3	Sasmita protocol	$NaIO_4$ in DMF at 150°C for 1 h under argon	60%	16%	4%
4	Manganese dioxide-based oxidation	MnO_2 in $CHCl_3$, reflux for 10 h	35%	43%	>10%
5	Kornblum oxidation	DMSO, $NaHCO_3$, 150°C for 8 h	53%	15%	<5%
6	Hass-Bender oxidation	2-Nitropropane, NaOMe, MeOH, reflux for 1 h	40%	31%	<5%
7	Ming protocol A	H_5IO_6, [C_{12}mim][$FeCl_4$], 50°C, 4 h	89%	Traces	0%
8	Ming protocol B	H_5IO_6, V_2O_5, [bmpy]PF_6, 70°C, 10 h	84%	Traces	0%
9	Chunbao approach	H_2O_2, V_2O_5, Boiling H_2O, Aliquat 336, 24 h	81%	Traces	0%
10	Pawar protocol	H_2O_2, PhosIL-BF_4, 50°C, 12 h	75%	Traces	Traces
11	IBX-mediated IL protocol	IBX, PhosIL-BF_4 and H_2O, 50°C, 12 h	72%	Traces	Traces
12	Khodaei method	$Bi(NO_3)_3.5H_2O$, molten TBAF, 100°C, 2 h	83%	Traces	0%

*All the products were separated and purified by flash column chromatography on silica gel, except for Ming protocols, in which recrystallization was carried out for purification. Isolated products were structurally characterized through ^{1}H-NMR and ^{13}C-NMR spectroscopy.

(3 × 20 mL). The organic layer was combined and treated with solution of 5% $NaHCO_3$ (3 × 20 mL) to become neutral and then washed with H_2O (3 × 20 mL). The liquid products were decontaminated via distillation, whereas solid product was decontaminated via recrystallization from EtOAc and n-hexane. The rest of the catalyst and IL were recovered through decantation of aqueous hydrogen organic halide produced in the reaction and concentration under *vacuo*. Under similar conditions, the recovered catalytic system was then reused.

2.10 General procedure of Chunbao approach for synthesis of dialdehydes

A mixture of organic dihalide (1 mmol), water (10 mL), hydrogen peroxide (30%, 6 mmol), vanadium pentoxide (0.02 mmol) and Starks' catalyst (0.2 mmol) was refluxed for an appropriate period of time (Tables 1 and 3). After reaction completion as indicated on TLC (solvent system of 10% EtOAc in hexane), the reaction mixture was allowed to cool at r.t and then the oil layer was separated. The crude mixture was decontaminated via silica gel-based chromatographic purification technique, in which ethyl acetate in hexane (1:2) as eluent was employed to afford desired product. The aqueous phase was reused under identical reaction conditions.

2.11 General procedure of Pawar protocol for synthesis of dialdehydes

A mixture of organic dihalide (2 mmol), (30%) H_2O_2 (30%, 12 mmol), PhosIL-BF_4 (4 mL) was stirred at temperature of 50°C under atmosphere of N_2 for suitable time (Table 1). After reaction completion as indicated on TLC (solvent system of 10% EtOAc in hexane), 50 mL of H_2O was poured. The mixture was extracted several times with EtOAc (3 × 10 mL). After removal of the ethyl acetate by rotary evaporator, the crude mixture was decontaminated via silica gel-based chromatographic purification technique, in which ethyl acetate in hexane (1:2) as eluent was employed to afford desired product. The layer of aqueous (aqueous what) was heated further at temperatures of 120°C to evaporate the H_2O and the residual IL was reused for numerous times without any change in its effectiveness.

2.12 General procedure of IBX-mediated IL protocol for synthesis of dialdehydes

A mixture of organic dihalide (2 mmol), IBX (6 mmol), PhosIL-BF_4 (4 mL) and H_2O (8 mL) was vigorously stirred at temperature of 50°C under atmosphere of N_2 for the appropriate period of time (Table 1). After reaction completion as indicated by TLC (solvent system of 10% EtOAc in hexane), the mixture was diluted with distilled H_2O and then extracted various times with Et_2O (3 x 20 mL). After removal of the ethyl acetate by rotary evaporator, the crude mixture was decontaminated via silica gel-based chromatographic purification technique, in which ethyl acetate in hexane (1:2) as eluent was employed to afford desired product. The aqueous layer was heated further at temperatures of 120°C to evaporate the H_2O and the residual IL was reused for numerous times without any change in its effectiveness [19].

2.13 General procedure of Khodaei method for synthesis of dialdehydes

To a round bottom flask of 100 mL containing molten tetrabutylammonium fluoride (2 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (4.4 mmol), the organic dihalide (2 mmol) was added. At temperature of 100°C, the mixture was vigorously stirred for appropriate period of time (Tables 1 and 3). The reaction progress was observed by TLC (solvent system of 10% EtOAc in hexane). After reaction completion, the mixture was cooled to room temperature and extracted several times with diethyl ether (3 x 20 mL). The organic layers were then combined and treated with H_2O. Drying was performed by using sulfate of soda. After removal of the diethyl ether by rotary evaporator, the crude mixture was decontaminated via silica gel-based chromatographic purification technique, in which ethyl acetate in hexane (1:2) as eluent was employed to afford desired product.

3 Spectral data of selected compounds

3.1 Spectral detail of 2,1,3-benzothiadiazole 5

Appearance: pale yellow solid; $\mathbf{R_f}$: 0.45 (*n*-hex: EtOAc (1:9)); **M.P**: 42-44°C; **^{1}H NMR** (300 MHz, DMSO): δ_H 7.60(dd, *J* = 3.2, 6.8 Hz, 2H), δ 8.02 (dd, *J* = 3.2, 6.8 Hz, 2H); **Anal. Calcd for** $C_6H_4N_2S$: C, 52.92; H, 2.96; N, 20.57; S, 23.55. Found: C, 52.93; H, 2.94; N, 20.55; S, 23.53.

3.2 Spectral detail of 4,7-bis(bromomethyl) benzo[c][1,2,5]thiadiazole 1

Appearance: white crystals; $\mathbf{R_f}$: 0.64 (*n*-hex: EtOAc (1:9)); **M.P**: 60-62°C; **^{1}H NMR** (300 MHz, DMSO): δ_H 4.97 (4H, s), 7.63 (2H, s); ^{13}**C NMR** (75 MHz, DMSO): δ_c 28.3, 129.6, 131.5, 153.8; **Anal. Calcd for** $C_8H_6Br_2N_2S$: C, 29.84; H, 1.88; Br, 49.63; N, 8.70; S, 9.96. Found: C, 29.82; H, 1.88; Br, 49.23; N, 8.69; S, 9.91.

3.3 Spectral detail of benzo[c][1,2,5] thiadiazole-4,7-dicarbaldehyde 2

Appearance: off-white solid; $\mathbf{R_f}$: 0.34 (*n*-hex: EtOAc (1:9)); **M.P**: 50-52°C; **IR** (cm^{-1}): 1772 (C=O); ^{1}**H NMR** (300 MHz, DMSO): δ_H 8.39 (s, 2 H), 10.90 (s, 2 H); ^{13}**C NMR** (75 MHz, DMSO): δ_c 130.6, 131.1, 154.1, 188.7; **Anal. Calcd for** $C_8H_4N_2O_2S$: C, 49.99; H, 2.10; N, 14.58; O, 16.65; S, 16.68. Found: C, 49.99; H, 2.09; N, 14.23; O, 16.64; S, 16.62.

3.4 Spectral detail of 3,3’-bis(bromomethyl)-2,2’-dihydroxy-1,l’-binaphthyl 12

Appearance: colorless solid; $\mathbf{R_f}$: 0.34 (*n*-hex: EtOAc (1:9)); **M.P**: 210-212°C; ^{1}**H NMR** (300 MHz, DMSO): δ_H 4.95 (dd, 4H); 6.98 (d, 2H), 7.25 (t, 2H), 7.31 (t, 2H), 7.92 (*d*, 2H), 8.14 (*s*, 2H), 8.28 (**s**, 2H) ^{13}**C NMR** (75 MHz, DMSO): δ_c 30.5, 114.2, 124.4, 125.0, 127.9, 128.4, 129.0, 129.7, 132.4, 135.5, 153.2; **Anal. Calcd for** $C_{22}H_{16}Br_2O_2$: C, 55.96; H, 3.42; Br, 33.85; O, 6.78. Found: C, 55.89; H, 3.41; Br, 33.81; O, 6.73.

3.5 Spectral detail of tris(4-formylphenyl) amine 18

Appearance: yellow solid; $\mathbf{R_f}$: 0.15 (*n*-hex: EtOAc (1:9)); **M.P**: 244-248°C; ^{1}**H NMR** (300 MHz, DMSO): δ_H 7.27 (*d*, J=7 Hz, 6H), 7.85 (d, J=8.5 Hz, 6H), 9.96 (*s*, 3H); ^{13}**C NMR** (75 MHz, DMSO): δ_c 124.55, 131.52, 132.59, 151.21, 190.51; **Anal. Calcd for** $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.25; O, 14.57. Found: C, 76.54; H, 4.60; N, 4.24; O, 14.54.

3.6 Spectral detail of anthracene-9,10-dicarbaldehyde 27

Appearance: dark-orange needles; $\mathbf{R_f}$: 0.78 (*n*-hex: EtOAc (1:9)); **M.P**: 236-237°C; ^{1}**H NMR** (300 MHz, DMSO): δ_H 11.43 (s, 2H), 8.78 (dd, *J* = 7.6, 3.7 Hz, 4H), 7.76 (dd, *J* = 7.0, 3.3 Hz, 4H); ^{13}**C NMR** (75 MHz, DMSO): δ_c 196.1, 131.6, 129.4, 128.3, 124.3; **Anal. Calcd for** $C_{16}H_{10}O_2$: C, 82.04; H, 4.30; O, 13.66. Found: C, 82.02; H, 4.29; O, 13.61.

4 Results and discussion

To compare the scope (yield, effectiveness and completeness) of well-known oxidative protocols for synthesis of dialdehydes from organic dihalides, studies have been used at wide level. In this investigation, twelve different methodologies were assessed by using 4,7-bis(bromomethyl)benzo[c][1,2,5]thiadiazole **1** as starting material (Figure 1). The evaluation results are illustrated in Table 1. **1** was synthesized by the two-step procedure of Mancilha et al. [13] and Page et al. [14], i.e., cyclization of *o*-phenylenediamine with $SOCl_2$ in the presence of Et_2O as base and DCM as solvent afforded benzothiazole **5** in 95% yield. In the next step, the synthesized benzothiadiazole **5** was bromomethylaed with trioxane and hydrobromic acid in the presence of H_2SO_4 and TTAB (Phase transfer catalyst) to furnish **1** in 92% yield (Scheme 1).

The synthesis of monoaldehydes from organic monohalides is well-documented using Sommelet reaction that offers remarkable advantages such as short reaction time, excellent yield, clean procedure and easy purification [20,21]. Moreover, this is one of the oldest techniques for the functionalization of organic halides and has been employed quite extensively for the synthesis of aldehydes from halomethyl compounds. In 2014, Xu et al. disclosed improved Sommelet reaction for the synthesis of monoaldehydes from organic monohalides. In the improved Sommelet

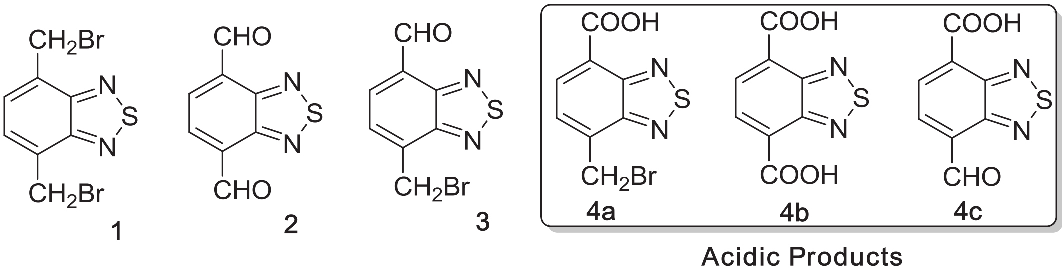
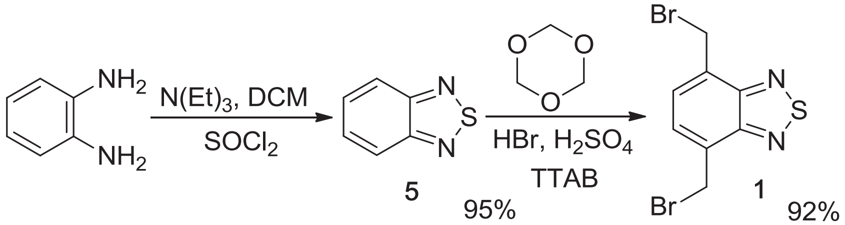


Figure 1: Structure of 2,1,3-benzothiadiazole derivatives.

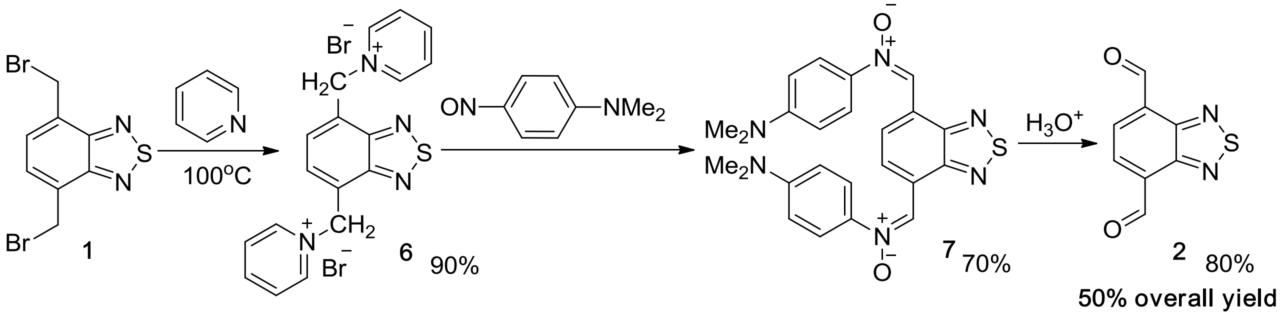
reaction hexamethylenetetramine (urotropin) in the presence of lanthanum triflate as catalyst in H_2O with sodium dodecyl sulfate as solubiliser was used [20,21]. To synthesized benzo[c][1,2,5]thiadiazole-4,7-dicarbaldehyde **2**, in our first investigation, improved Sommelet reaction was employed (Table 1, Entry 1) [20]. This protocol provided **2** in 65% yield with the formation of **3** in 12% yield and traces of acidic products (Figure 1). In the next investigation, popular and important name reaction *viz.* Kröhnke oxidation, which is also one of the oldest name reactions, was studied [22]. Kröhnke oxidation is related with Sommelet reaction, here the oxidizing reagent is a combination of pyridine and *N*,*N*-dimethyl-4-nitrosoaniline. The individual pathways are (i) substitution of the halide **1** with pyridine to deliver **6** (90%), (ii) reaction of **6** with *N*,*N*-dimethyl-4-nitrosoaniline to obtain **7** (70%) and (iii) acid hydrolysis of **7** to yield **2** (80%) in overall yield of 50% (Scheme 2). However, the result reveals that the Kröhnke oxidation is inferior to the Sommelet reaction, i.e., it provides **2** in 50%, **3** in 18% and the yield of acidic products is greater than 10% (Table 1, Entry 2) [22].

Next, the scope of Sasmita protocol was investigated. For this investigation, sodium metaperiodate ($NaIO_4$) in dimethyl formamide (DMF) at mild reaction conditions (150°C for 60 min under argon atmosphere) was used [23]. In this methodology, yields of **2**, **3** and acidic products were 60%, 16% and 4%, respectively (Table 1, Entry 3). In next study, MnO_2 in refluxing CH_3Cl for 10 h was used [24]. It is well-documented that manganese dioxide is an inexpensive, convenient and readily available oxidant [25]. However, in our examination, this method was found to be highly unsuitable for synthesis of dialdehydes from organic dihalides, i.e., it provides only 35% of **2** (the poorest) along with the formation of **3** and acidic products in 43% and >10% yield, respectively (Table 1, Entry 4). In next case, Kornblum oxidation was employed. This is perhaps the most extensively employed and best-known technique for the organic halides oxidation [26,27]. This reaction was performed in dimethyl sulfoxide (DMSO) in the presence of sodium bicarbonate at 150°C for 8 h [28]. Unfortunately, this reaction also provided unsuitable yield of **2** (53%) with formation of mono-product **3** (15%) and acidic products (5%) (Table 1, Entry 5). After examining the Kornblum oxidation, we moved towards the examination of Hass-Bender oxidation approach [29,30]. The reaction was performed in 2-nitropropane in the presence of NaOMe, refluxing in methanol for 1 h. The yield of **2** in this case was also poor (40%) and the reaction led towards formation of mono-product (31%) and acidic products (<5%) (Table 1, Entry 6).

After assessing the classical approaches, we moved towards the investigation of green processes. Significant characteristics of ILs based green processes in this context include non-flammability, efficient recyclability, high thermal stability and low volatility. In recent years, ILs have achieved significant consideration owing to their valuable physicochemical characteristics



Scheme 1: Synthesis of bis(bromomethyl)benzo[c][1,2,5]thiadiazole.



Scheme 2: Application of Kröhnke oxidation for synthesis of dialdehyde.

including chemical stability and high ion conductivity [31,32].

In first two cases, two related H_5IO_6-based green IL methods (Ming protocols) were tested. In first case, H_5IO_6 in ionic liquid *viz.* 1-dodecyl-3-methylimidazolium iron chloride [C_{12}mim][FeC_{14}] under mild reaction conditions (50°C, 4 h) was employed (Table 1, Entry 7) [33], while in second case, H_5IO_6 catalyzed by vanadium peroxide (V_2O_5) in ionic liquid *viz.* 1-butyl-3-methylimidazolium hexafluorophosphate [bmpy][PF_6] under mild reaction conditions (70°C, 10 h) was employed (Table 1, Entry 8) [34]. Both approaches provided **2** in excellent yield, i.e., 89% and 84%, respectively with traces of only **3** and no acidic products. The observed striking features of these two ionic liquid methodologies are that no traces of over-oxidation to acids were observed, separation of synthesized product was very simple, handling of catalytic system was also very simple and can be reused or recycled (approximately 20 times) without any important loss of catalytic efficiency (Table 2). Moreover, these procedures display many exclusive physicochemical characteristics, for instance, wide electrochemical window, large liquid range, large thermal stability, excellent capacity to dissolve many chemicals and negligible nonflammability and volatility under ambient conditions. After determining the scope of H_5IO_4-based approach, we moved forward to study H_2O_2-based procedures (Chunbao approach and Pawar protocol). In case of Chunbao approach (a green method), hydrogen peroxide (H_2O_2) catalyzed by vanadium oxide (V_2O_5) and Starks' catalyst (Aliquat 336) in boiling water for 24 h were employed (Table 1, Entry 9) [35]. This approach, was attributed to high stability, inexpensive, presence of high oxygen contents and H_2O_2 was used as oxidizer. The catalysts (V_2O_5 and Starks' catalyst) are also cheap, stable and effective and can be reused for several times with only a minor change in its effectiveness (Table 2). Moreover, in this transformational approach, only H_2O was employed for diluting the H_2O_2 and beauty of this approach was that, in the whole process, no organic solvents were employed. Water and hydrochloric acid were the two waste products in reaction. The yield in the case of **2** was observed to be very good (81%) along with traces of 3 only and without acidic product. In the next case, Pawar technique was employed, H_2O_2 in trihexyl(tetradecyl)phosphonium tetrafluoroborate (PhosILBF_4), a highly basic phosphonium IL, at 50°C for 12 h [36]. As the density of phosIL-BF_4 is less than H_2O, the product was isolated only through decanting the aqueous layer. This technique provided **2** in 75% yield with formation of traces of acidic products and **3** (Table 1, Entry 10). The next methodology is very much related with previous one. In this approach, IBX in phosphonium IL (PhosIL-BF_4) and water at 50°C for 12 h was employed [37]. *O*-Idoxy benzoic acid (IBX) was used as oxidizer on account of its efficient, selective, mild and ecofriendly characteristics and operational simplicity. The yield of **2** in this process was observed to be excellent (83%) with only traces of **3** and acidic products (Table 1, Entry 11). In the case of Pawar procedure and IBX-mediated IL process, the phosphonium IL could be recycled for several time with only a minor change in its effectiveness (Table 2). The last technique under evaluation was $Bi(NO_3)_3{\cdot}5H_2O$-based approach (Khodaei method) [38]. Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) is a commercially available, crystalline solid and inexpensive reagent and requires no superior handling. In this process, $Bi(NO_3)_3{\cdot}5H_2O$ was employed as catalyst in TBAF as ionic liquid at 100°C for 2 h. TBAF could be reused or recycled for approximately 5 times (Table 2). The yield in this case was excellent (83%) with only traces of 2 without any acidic products (Table 1, Entry 12).

The result of investigation revealed that generally the green protocols are eco-friendlier and highly efficient as compared to classical protocols. In classical approaches, none of them provides excellent yield. However, in green

Table 2: Efficiency of recycled ionic liquids or catalysts in synthesis of 2.

Entry	IL or catalyst	Reactant	Product	Yield (%) of recovered IL or catalysts			
				Cycle 1	Recycle 1	Recycle 2	Recycle 3
1	[C_{12}mim][$FeCl_4$]	1	2	89%	88%	88%	85%
2	[bmpy]PF_6]	1	2	84%	84%	84%	84%
3	V_2O_5 and Starks' catalyst	1	2	81%	80%	80%	80%
4	PhosIL-BF_4	1	2	75%	72%	72%	71%
5	PhosIL-BF_4	1	2	72%	71%	70%	70%
6	TBAF	1	2	83%	70%	65%	65%

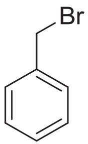
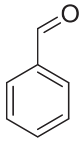
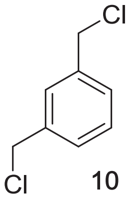
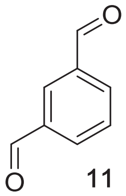
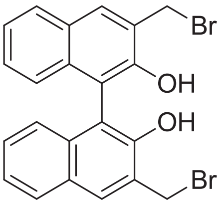
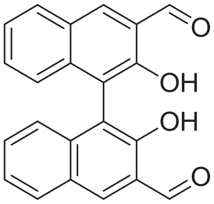
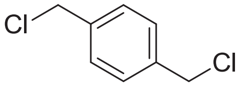
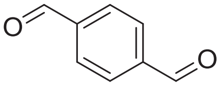
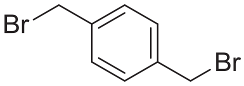
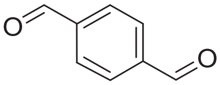
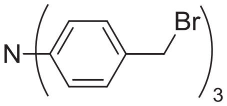
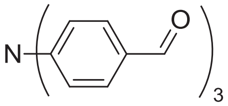
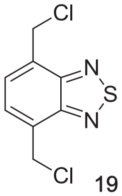
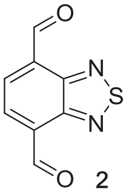
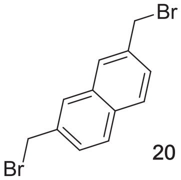
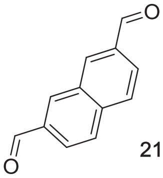
techniques, i.e., Pawar protocol and IBX-mediated IL process provide excellent yield (>70%) while the Ming methodology, Chunbao approach and Khodaei method provide outstanding yields (>80%). Hence, the most promising approaches were Ming protocol, Chunbao approach and Khodaei method, which were selected for further investigation.

Further, to evaluate the extent of selected approaches toward synthesis of different significant dialdehyde and trialdehyde precursors, the selected approaches were applied on numerous bromo- and chloro-precursors. The results of investigation are illustrated in Table 3. Application of four selected protocols on organic halides (**8**, **10**, **12**, **14**, **16**, **17**, **19**, **20**, **22**, **24**, **26**, **28** and **30**) led to the formation of aldehydes (**9**, **11**, **13**, **15**, **18**, **2**, **21**, **23**, **25**, **27** and **29**) respectively. Indeed, numerous functionalized organic dihalides containing electron-withdrawing or electron-donating groups in the *meta*- or *para*-positions were efficiently transformed to dialdehydes. From the isolated yields of oxidation of **14** and **16** and of **28** and **30**, it appears that relatively more yields were produced by dichloro compounds then that by dibromo compounds. Also, Ming protocols A and B demonstrated more yields in the case of *meta*-substituted groups (for example **10**), while Chunbao and Khodaei approaches demonstrated more yields in the case of *para*-substituted groups (for example **14**). The reaction conditions of selected oxidative protocols were mild enough to induce any damage to the acid-sensitive moieties (for example **12**). The oxidation of nitrogen moiety is very common when compounds like **28** and **29** are subjected under oxidative conditions; however, the selected oxidative protocols did not lead to oxidation of nitrogen moiety of **28** and **29**. a,ß-Halomethyl compounds (for example **22**) were also reacting in high yields using this procedure without the formation of any intramolecular condensation based by-products. Bulky substrates (for example **12**) were easily reacted in short reaction times with good to excellent isolated yields.

Overall, Ming protocol A offered yield in the range of 82-96%, Ming protocol B provided yield in the range of 75-92%, Chunbao approach delivered yield in the range of 71-85% and Khodaei method in the range of 70-90%. Overall, during investigation, all selected protocols demonstrated excellent yield but the Ming protocol A was observed to be outstanding in all the cases (Table 3).

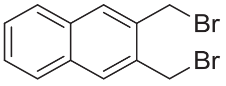
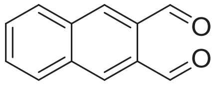
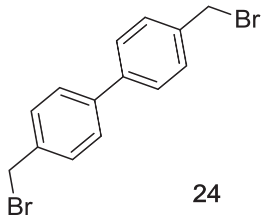
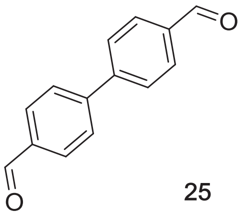
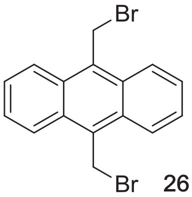
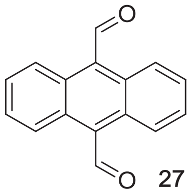
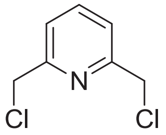
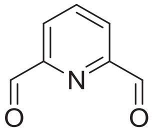
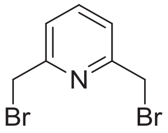
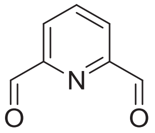
The plausible mechanisms of investigated oxidative protocols are outlined in Scheme 3. In the case of Sasmita protocol, DMF enhances the nucleophilicity of $NaIO_4$. The DMF-$NaIO_4$ based nucleophile **31** attacks on positively charged (electrophilic) carbon of halomethyl group, leading to formation of intermediate **32** and bromine ion. Afterwards, the resulting Br^- ion processes as the base in the elimination reaction to furnish the carbonyl entity. When it comes to manganese dioxide-based oxidation, under refluxing conditions, the halide of halomethyl group is thermally displaced to produce a benzyl radical **33** via activated interaction with MnO_2, which instantly couples with the radical of oxygen of **34** to produce an intermediate **35**. This intermediate subsequently undergoes abstraction of acidic hydrogen, followed by reductive breakage of oxygen-manganese bond in **35** with abstraction of OMnX, leading to development of organic aldehydes and MnO as a salt Mn(X)OH. Where Chunbao approach is concerned, V_2O_5 can exist as VO_2^+ and VO_3^- in acidic solution. Addition of H_2O_2 to VO_2^+ can give the red oxoperoxo $VO(O_2)^+$ **36** and the yellow oxodiperoxo $VO(O_2)_2^-$ moieties **37**, which reacts with organic halide to produce transition state **38** and then, **38** eliminate the oxoperoxo **36** and proton to afford the desired product. As for Ming protocol, in acidic solution, V_2O_5 can exist as VO_2^+ and VO_3^- at first. Addition of H_2O_2 to VO_2^+ can give the red oxoperoxo $VO(O_2)^+$ **36** and the yellow oxodiperoxo $VO(O_2)_2^-$ moieties **37**, which reacts with halide to produce transition state **38** and then, **38** eliminated the oxoperoxo **36** and proton to afford the required aldehyde or ketone. The low potencies of the secondary organic halides may be due to steric hindrances of the $VO(O_2)_2^-$ **37**, and which reveals that $VO(O_2)_2^-$ **37** is a bulky nucleophile, and hence is sensitive towards steric hindrance. The answer of the question that why the reaction of benzyl chlorides is faster than benzyl bromides is that $VO(O_2)_2^-$ **37** is a good leaving group, and hence it is substituted more easily by the better nucleophile, Br^-, then by the Cl^-. It seems like that the development of **38** between **37** and organic halide is the rate-determining step. With regards to Kornblum oxidation, the oxygen atom on **39** is partially negatively charged and can act as a nucleophile. Under temperature conditions, the nucleophilic oxygen of **39** attacks on positively charged (electrophilic) carbon of halomethyl group, leading to formation of intermediate **40**. This intermediate **40** experiences subsequently loss of acidic hydrogen, followed by reductive breakage of oxygen-sulfur bond resulting in the formation of aromatic aldehydes and Me_2S, H_2O, CO_2 and KBr as byproducts. Turning to Hass-Bender oxidation, deprotonation on 2-nitropropane **41** by NaH results in the formation of powerful nucleophile, which attacks on positively charged (electrophilic) carbon of halomethyl group to

Table 3: Application of selected oxidative protocols for synthesis of dialdehydes.

Entry	Substrates	Products	Protocols	Time and temp	Yields
1	 8	 9	Ming protocol A	2 h, 30°C	96%
			Ming protocol B	3 h, 50°C	92%
			Chunbao approach	14 h, reflux	81%
			Khodaei method	1.5 h, 100°C	84%
2	 10	 11	Ming protocol A	2.5 h, 40°C	89%
			Ming protocol B	6 h, 50°C	86%
			Chunbao approach	24 h, reflux	85%
			Khodaei method	2 h, 100°C	90%
3	 12	 13	Ming protocol A	4 h, 50°C	85%
			Ming protocol B	10 h, 70°C	82%
			Chunbao approach	24 h, reflux	72%
			Khodaei method	2 h, 100°C	77%
4	 14	 15	Ming protocol A	2.5 h, 40°C	92%
			Ming protocol B	5 h, 50°C	91%
			Chunbao approach	12 h, reflux	80%
			Khodaei method	2 h, 100°C	89%
5	 16	 15	Ming protocol A	2.5 h, 40°C	91%
			Ming protocol B	4 h, 50°C	88%
			Chunbao approach	12 h, reflux	72%
			Khodaei method	2 h, 100°C	81%
6	 17	 18	Ming protocol A	4 h, 50°C	82%
			Ming protocol B	12 h, 70°C	81%
			Chunbao approach	24 h, reflux	75%
			Khodaei method	2 h, 100°C	70%
7	 19	 2	Ming protocol A	4 h, 50°C	89%
			Ming protocol B	12 h, 70°C	87%
			Chunbao approach	24 h, reflux	87%
			Khodaei method	2 h, 100°C	89%
8	 20	 21	Ming protocol A	4 h, 40°C	91%
			Ming protocol B	10 h, 50°C	82%
			Chunbao approach	20 h, reflux	83%
			Khodaei method	2 h, 100°C	81%

(*Continued*)

Table 3: (Continued)

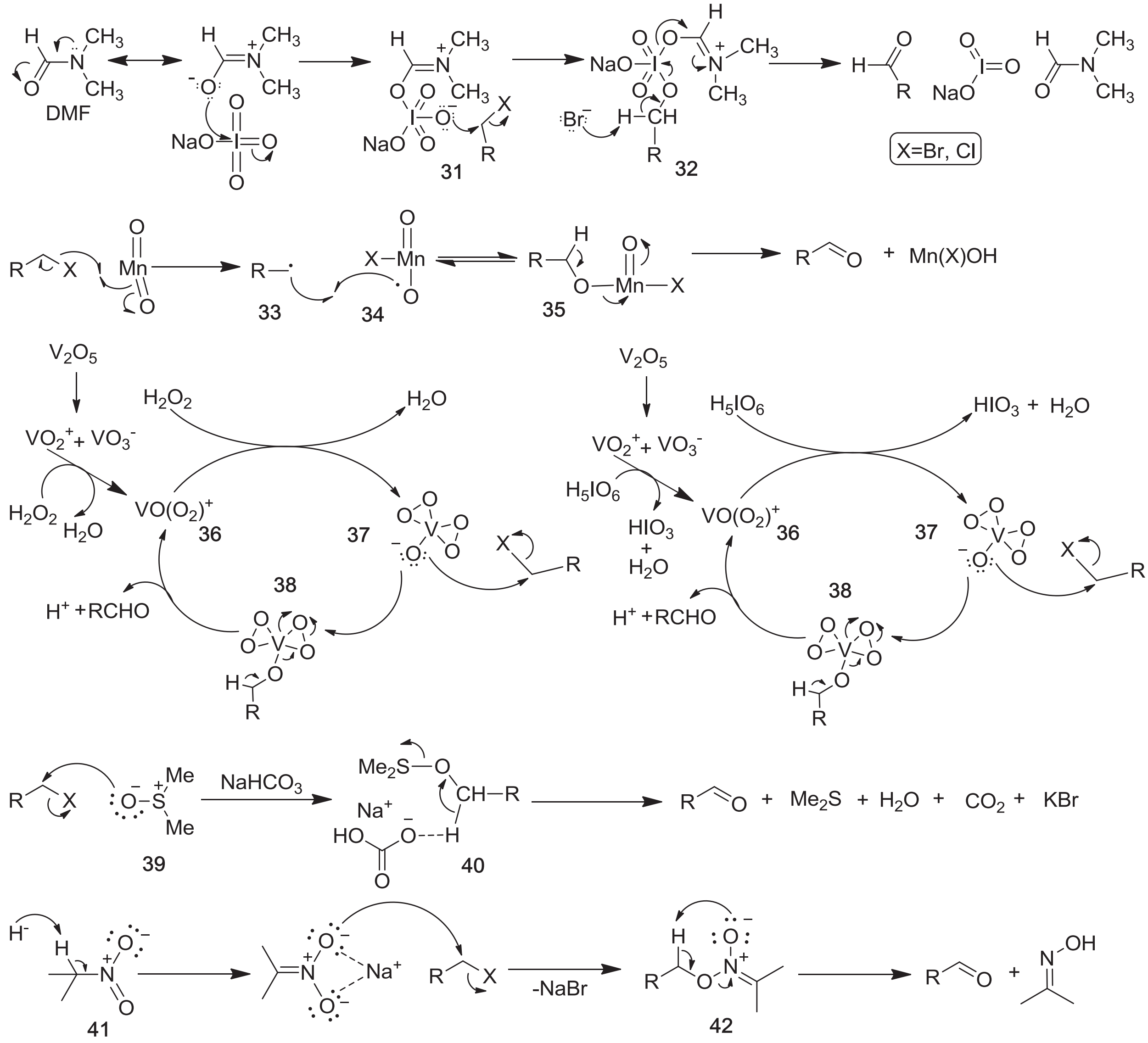
Entry	Substrates	Products	Protocols	Time and temp	Yields
9	 22	 23	Ming protocol A	3.5 h, 40°C	91%
			Ming protocol B	5 h, 50°C	83%
			Chunbao approach	20 h, reflux	81%
			Khodaei method	2 h, 100°C	80%
10	 24	 25	Ming protocol A	2.5 h, 40°C	87%
			Ming protocol B	6 h, 50°C	83%
			Chunbao approach	20 h, reflux	80%
			Khodaei method	2 h, 100°C	83%
11	 26	 27	Ming protocol A	2.5 h, 40°C	85%
			Ming protocol B	5 h, 50°C	81%
			Chunbao approach	20 h, reflux	80%
			Khodaei method	2 h, 100°C	91%
12	 28	 29	Ming protocol A	2 h, 40°C	83%
			Ming protocol B	3 h, 50°C	80%
			Chunbao approach	20 h, reflux	71%
			Khodaei method	2 h, 100°C	79%
13	 30	 29	Ming protocol A	2 h, 40°C	83%
			Ming protocol B	3 h, 50°C	75%
			Chunbao approach	20 h, reflux	68%
			Khodaei method	2 h, 100°C	75%

*In the case of Chunbao and Khodaei methods, all the products were separated and purified by flash column chromatography on silica gel, while in case of Ming protocols, all the products were separated and purified recrystallization. Isolated products were structurally characterized through ^{1}H-NMR and ^{13}C-NMR spectroscopy.

deliver intermediate **42**. The subsequently abstraction of acidic hydrogen, followed by reductive breakage of oxygen-nitrogen bond in **42** leading to the development of organic aldehydes.

5 Conclusion

In this research work, various classical and green techniques were assessed for their effectiveness towards synthesis of dialdehydes from organic dihalides. The classical approaches under observation include modified Sommelet oxidation (urotropin in the presence of sodium dodecyl sulfate and La(OTf)$_2$), the Kröhnke oxidation (Py followed by *N*,*N*-dimethyl-4-nitrosoaniline and subsequent acid treatment), Sasmita protocol (NaIO$_4$ in DMF), manganese dioxide-based oxidation (MnO$_2$ in CHCl$_3$), Kornblum oxidation (DMSO in the presence of NaHCO$_3$) and Hass-Bender oxidation (2-Nitropropane in the presence of NaOMe and MeOH), while the green approaches include Ming protocol A (H$_5$IO$_6$ in [C$_{12}$mim][FeCl$_4$] as IL), Ming protocol B (H$_5$IO$_6$ and V$_2$O$_5$ in [bmpy]PF$_6$ as IL), Chunbao procedure (H$_2$O$_2$ in presence of V$_2$O$_5$ and Aliquat 336), Pawar method (H$_2$O$_2$ in PhosIL-BF$_4$ as IL), IBX-mediated IL process (IBX in PhosIL-BF$_4$) and bismuth nitrate-based IL technique (Bi(NO$_3$)$_3$.5H$_2$O in TBAF as IL). In this assessment the yield, overoxidation towards acidic products, cost-effectiveness, eco-friendliness and recyclability are the main parameters



Scheme 3: Plausible mechanistic pathways for formation of synthesis of dialdehydes from organic dihalides.

which are under observation. Research reveals that green approaches are superior to classic approaches. Among green techniques Ming protocols, Chunbao approach and Khodaei method are highly efficient due to the following reasons: (i) they provide outstanding yields (>80%) in most cases, (ii) they do not lead towards overoxidation, (iii) they are highly recyclable without any important loss of catalytic efficiency, (iv) they have excellent capacity to dissolve many chemicals, (v) possess nonflammability and large thermal stability, (vi) have volatility under ambient conditions, (vii) they are inexpensive, (viii) eco-friendlier, and (xi) require no special handling (easy work-up). The most superior observed approach is Ming protocol A because upon applying it on numerous bromo- and chloro-precursors, it demonstrates outstanding yield (>82%) in all cases. This research work also highlights that more research is required to modify classical methodologies to green approaches. The purpose of this effort is to help chemist in carrying out routine operations in organic synthesis in a laboratory. This research is fruitful to get knowledge about recent synthesis techniques, to select finest synthetic approach, to develop further new transformational methodologies and to improve current transformational approaches (by modifying classical methods to green approaches). This work delivers a strong platform that provides a way to conduct further research in this field and investigate additional hypotheses. We hope that the results of our work will offer a strong motivation for further research progress.

Supplementary material: Spectral data of the prepared compounds are given in the Supplementary material to this paper.

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Conflict of interest: The authors declare that they have no conflict of interest.

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