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Basic Ionic Liquid [Bmim]OH as Efficient Greener Medium for the Oxidation α -Hydroxy Ketone Compounds and Alcohols to Carbonyl Compounds with Potassium Permanganate

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In this work, a convenient and greener procedure for synthesizing 1,2-diarylethane-1,2-dione derivatives as well as the oxidation of primary and secondary alcohols was explored using an oxidizing agent (KMnO_4) in a basic ionic liquid of 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH) as greener medium. The selective oxidation of α -hydroxy ketone compounds together with primary and secondary alcohols in the presence of KMnO_4 in [Bmim]OH afforded corresponding carbonyl compounds of 1,2-diarylethane-1,2-dione derivatives and aldehydes or ketones in high yields (85-97% and 83-97%, respectively). The reactions are mild, fast, and efficient. Moreover, KMnO_4 in [Bmim]OH medium was easily recovered and reused for at least four additional reactions without significant loss of efficiency with a consistent yield of about 80%.

Graphical abstract



Keywords

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1. Introduction

Over the past decade, ionic liquids (ILs) have attracted much attention due to their special properties; they are “designer solvents” [1], as their physical properties such as melting point, viscosity, density, hydrophilicity, and hydrophobicity can be modified according to the nature of the desired reactions by altering the nature of their cations and

anions [2], resulting in almost undetectable vapor pressure, excellent chemical stability, high thermal stability, wide liquid temperature range and strong solvent power for a wide range of organic, inorganic and polymeric molecules. Some ILs have been successfully used as the media in many chemical reactions [3-4].

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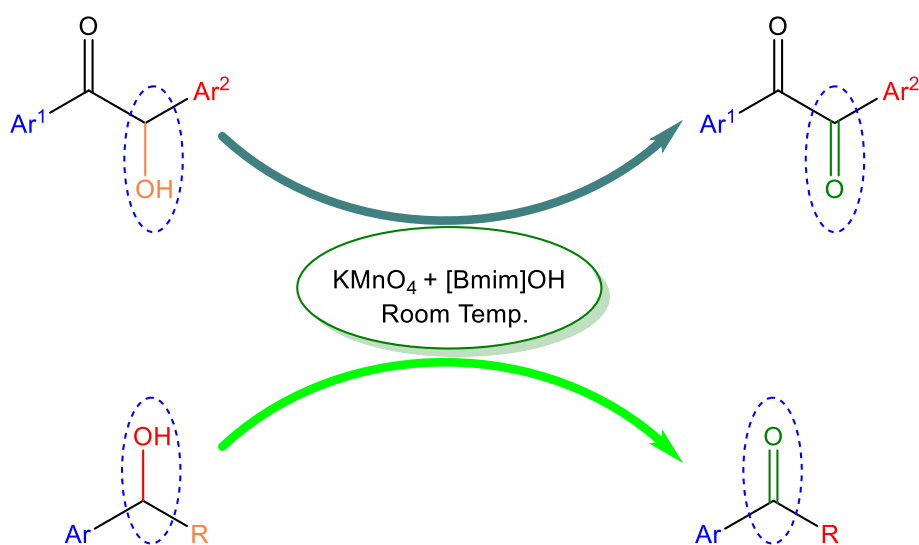
In recent years, a basic ionic liquid (IL) namely 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH) has received a great deal of attention as possible "green" and more used in organic reactions to replacement for volatile organic solvents. In addition, it has been used as a catalyst and reaction medium in many important reactions such as Michael addition [5], Knoevenagel condensation [6-7], Markovnikov addition [8], benzoin condensation and Stetter reaction [9], hydrocarboxylation of alkynyl nitriles [10], synthesis of pyrazoloimidazole-2-thione-*N*-nucleosides [11], synthesis of oximes [12], synthesis of mono and bis spirooxindole derivatives [13], etc.

The partial oxidation of primary and secondary alcohols to corresponding aldehydes and ketones is a fundamental synthetic transformation in organic chemistry that is industrially important [14-16]. Various oxidants such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [17], ruthenium(III) chloride (RuCl₃) [18], ion-supported hypervalent iodine(III) reagent [19], chromium trioxide (CrO₃) [20] and potassium permanganate (KMnO₄) [21] have been used in ILs. These conditions are environmentally benign or have good selectivity. In addition, some of these reaction mixtures can be recyclable.

The formation of dibenzoyl or benzil derivatives (diphenylethanedione) (PhCO)₂ by oxidation of α -hydroxy ketone, also known as acyloins, has been extensively studied for the production of fine chemicals [28-33]. 1,2-Diarylethane-

1,2-diones have received a great deal of attention because of their photoluminescence properties [34-35], photochemical reactions [36], antioxidant activity [37-38], and potential application as inhibitors of acid corrosion of mild steel and photosensitive agents in photocurable coating [39]. Moreover, these compounds constitute useful intermediates in organic synthesis as precursors of various homo- and heterocyclic compounds [40-48] as well as multi-dentate ligands for coordination chemistry [49-51].

Previously, we reported the utilization of ILs as a green reaction medium such as benzoin condensation catalyzed by *N,N*-dimethylbenzimidazolium iodide and NaOH under green conditions (i.e., neutral ionic liquid [Bmim]PF₆, in water, and under solvent-free) [52] and benzoin condensation and stetter reaction catalyzed by *N,N*-dimethylbenzimidazolium iodide in [Bmim]OH [9]. Moreover, ionic liquid 1-butyl-3-methylimidazolium bromide ([Bmim]Br) can be used as both solvent and catalyst for a green reaction of cross benzoin condensation [53]. Herein we report our extended investigation of potassium permanganate (KMnO₄) as an efficient oxidative reagent for α -hydroxy ketone derivatives leads to 1,2-diarylethane-1,2-dione derivatives, including alcohols derivatives to their corresponding carbonyl compounds (aldehydes and ketones) in basic ionic liquid namely [Bmim]OH (Scheme 1). Moreover, the recycling of the mixture of oxidative reagent (KMnO₄) and basic ionic liquid ([Bmim]OH) was also investigated.



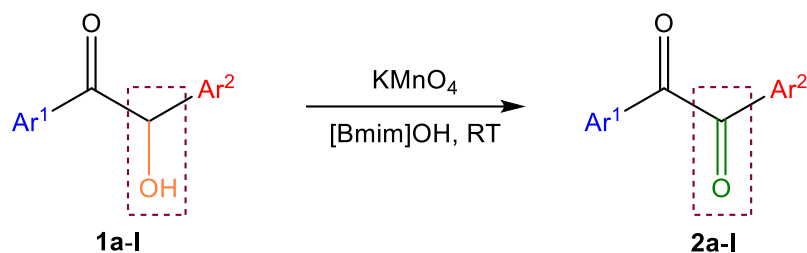
Scheme 1. Selective oxidation of α -hydroxy ketone derivatives and alcohols leads to the corresponding 1,2-diarylethane-1,2-dione and carbonyl compound derivatives.

2. Results and Discussion

In this work, reaction conditions for selective oxidation of substrate α -hydroxy ketone derivatives **1a-l** and alcohols **3a-k** were firstly surveyed, which was carried out under similar conditions as reported in the literature [21] except 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH) was used as green solvent at room temperature (Tables 1 and 2).

Under this condition, selective oxidation using KMnO₄ as an oxidizing reagent in green solvent ([Bmim]OH), gives a good yield (90%) of 1,2-diphenylethane-1,2-dione (**2a**) from simple α -hydroxy ketone namely benzoin (**1a**) (Table 1) that

was comparable with previously reported by Kumar and co-workers for the synthesis of **2a** (89%) in the presence of [Bmim]BF₄ within 90 min [21]. The obtaining different results for α -hydroxy ketones show that derivatives with electron-withdrawing substituents have been oxidized faster and in higher yield (91-96%) than others (i.e., **1b**, **1e**, **1g**, **1i-j**, and **1l**). Electron-donating substituents on the aromatic ring of α -hydroxy ketone compounds (**1c-d**, **1h**, and **1k**) slightly decreased the yields of 1,2-diarylethane-1,2-dione products and slightly increased reaction times, however in comparison with a heteroatom (furoin **1f**), was oxidized very fast and to give 1,2-di-2-furanyl-1,2-ethanedione (**2f**) in excellent yield (97%) (Table 1, entry 6).

Table 1. Oxidation of α -hydroxy ketone derivatives with KMnO_4 in $[\text{Bmim}]\text{OH}$ at room temperature.

Entry		Ar ¹	Ar ²	Time (min)	Yield (%)
1	1a			90	90 (2a)
2	1b			60	94 (2b)
3	1c			110	88 (2c)
4	1d			120	85 (2d)
5	1e			60	96 (2e)
6	1f			40	97 (2f)
7	1g			60	93 (2g)
8	1h			100	89 (2h)
9	1i			80	92 (2i)
10	1j			90	91 (2j)
11	1k			120	87 (2k)
12	1l			50	95 (2l)

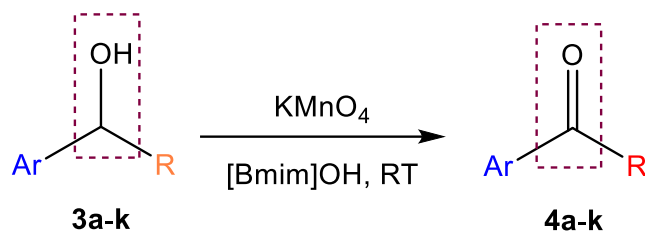
In addition, we have investigated on oxidation system of alcohols in similar conditions [21], a wide variety of alcohols (primary and secondary alcohols of **3a-g** and **3h-k**, respectively) leads to their corresponding aldehydes **4a-g** and ketones **4h-k** in high yields within less than 1 hour (Table 2).

The obtaining results from this experiment (Table 2), show that the use of oxidative reagent (KMnO_4) with ionic liquid ($[\text{Bmim}]\text{OH}$) causes the faster oxidation of benzylic alcohols **3a-c** and **3f** (30-45 min.) with higher yields of aldehydes **4a-c** and **4f** (91-95 and 97%). Similar results to table 1, electron-

donating substituents (such as Me, OMe, or OH groups) on the aromatic ring of benzylic alcohols (**3d-e**, including **3g**) slightly decreased the yields of aldehyde products and slightly increased reaction times. The obtained results are consistent with earlier research on benzylic alcohols in the presence of $[\text{Bmim}]\text{Br}$, which demonstrated that derivatives with electron-withdrawing substituents were oxidized more quickly and with higher yields than compounds with electron-donating substituents [54]. In contrast, results utilizing $[\text{Bmim}]\text{BF}_4$ showed that electron-withdrawing benzylic alcohols require a longer reaction time than the other types [21].

Table 2. Conversion of primary and secondary alcohols to the corresponding carbonyl compounds in the presence of KMnO_4 and

[Bmim]OH at room temperature.



Entry		Ar	R	Time (min)	Yield (%)
1	3a		H	40	91 (4a)
2	3b		H	35	93 (4b)
3	3c		H	30	95 (4c)
4	3d		H	40	89 (4d)
5	3e		H	40	87 (4e)
6	3f		H	30	97 (4f)
7	3g		H	40	88 (4g)
8	3h		CH ₃	45	85 (4h)
9	3i		CH ₃	45	87 (4i)
10	3j		CH ₃	45	86 (4j)
11	3k			55	83 (4k)

The oxidation using potassium permanganate in [Bmim]OH in the presence of secondary alcohols **3h-k** as precursor gave good yields of ketones **4h-k** (83-87%) in 45-50 min. The yield of the product **4k** was slightly lower (83%) and reaction time longer as compared with those in products **4h-j**. This may be due to the steric effect of two phenyl groups between carbonyl in alcohol **3k**. In comparison to other solvents previously employed, acetonitrile (CH₃CN) provided slightly lower product yields for the oxidation of primary and secondary alcohols by KMnO₄ and required a longer reaction time (90 min.) in some cases, such as the formation of acetophenone (**4h**). However, when dichloromethane (CH₂Cl₂) was used as the solvent, the reactions required a significantly

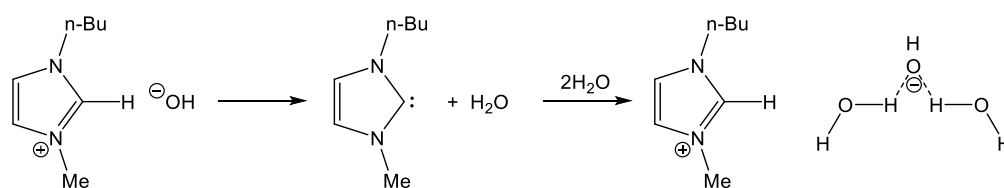
longer time and low product yields were obtained [55]. Additionally, numerous solvents and catalysts were employed in these prior processes.

Subsequently, the efficient recyclability of the used [Bmim]OH as a green solvent containing the KMnO₄ was demonstrated for the oxidation of α -hydroxy ketone derivatives and alcohols leading to 1,2-diphenylethane-1,2-diones and aldehydes or ketones. We were examined for the oxidation reaction of α -hydroxy ketone (**1a**) and benzyl alcohol (**3a**) in a mixture solution of KMnO₄ and [Bmim]OH. After the first run of **1a** and **3a**, which gave 1,2-diphenylethane-1,2-dione (**2a**) and benzaldehyde (**4a**) in 90 and 91% yields, the KMnO₄ in the presence of [Bmim]OH after extraction separation was

reused without any treatment due to the formation of metal-carbene complex (see mechanism) in the same type of reaction for at least four cycles.

The recovered KMnO_4 in $[\text{Bmim}]\text{OH}$ was subjected to a second cycle with 1 equiv. of substrate **1a** gave 1,2-diphenylethane-1,2-dione (**2a**) in 88% yield. Similarly, in the third, fourth, and fifth cycles, the yield of 1,2-diphenylethane-1,2-dione product was 85%, 83%, and 80%, respectively, and in the second cycle of substrate **3a** with 1 equiv. gave benzaldehyde (**4a**) in 89% yield. Similarly, in the third, fourth, and fifth cycles, the yield of aldehyde products was 86%, 84%, and 81%, respectively (Table 3). Our results shown in table 3, demonstrated that this oxidative system was readily recyclable for at least four runs without any significant loss of catalytic activity.

The slight decrease in the yield may be due to the conversion of hydroxide ion to water which the hydroxide ion plays an important role in deprotonating the C2-hydrogen of imidazolium ring of 1-butyl-3-methylimidazolium (Bmim) and



Scheme 2. The behavior of $[\text{Bmim}]\text{OH}$ in the absence and presence of water, based on [24].

The mechanism of the oxidation in the combination of KMnO_4 and $[\text{Bmim}]\text{OH}$ probably involves the formation of *N*-heterocyclic carbene of Bmim imidazolium ring and the formation of metal-carbene complex (Scheme 3), which can be explained by the following steps. The first step involves deprotonation of the imidazolium ring of Bmim at C2-hydrogen by a hydroxide ion [56]. The generated carbene acts as a strong ligand to electrophilic metal center of KMnO_4 to form a metal-carbene complex. This process also means the direct oxidative addition of imidazolium cation to a metal center [54]. The metal-carbene complex catalyst oxidizes alcohols, producing the oxidation products **2a-l** and **4a-k**. Deprotonation by a hydroxide ion led to the regeneration of an active metal-carbene complex.

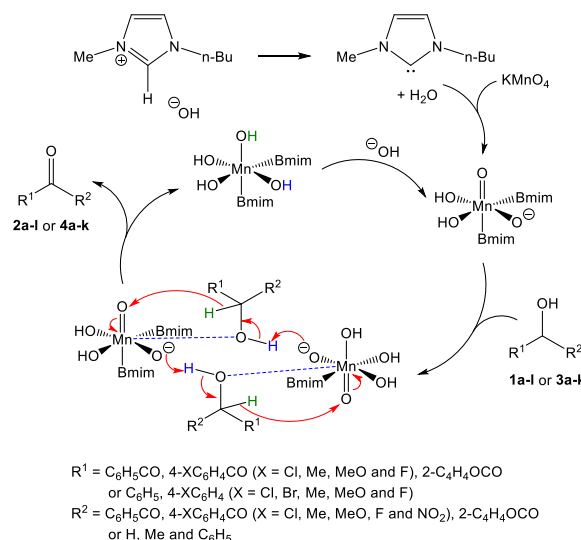
Both steric and electronic variables are involved in this oxidation process. When the steric hindrance of alcohols is increased, the rate of reaction is reduced due to the steric effect of alcohols and Bmim ligands, as was the case when α -hydroxy ketone and secondary alcohols took longer to react than benzylic alcohols in the oxidation reaction. During the oxidation process of alcohols, proton of hydroxy of alcohol can be abstracted by oxide of metal-carbene complex which can generate alkoxide intermediate, therefore alcohol with electron-withdrawing substitutes can stabilize them better than electron-donating substitutes, resulting in a faster reaction time and higher product yield. In contrast, ionic liquids with weakly coordinating, inert anions, such as BF_4^- , only serve as solvents in transition metal catalysis [54] and do not function as ligands like in this mechanism. As such, the mechanism involves the nucleophilic attack of alcohol lead to electron-donating groups increase the yield of oxidation products in shorter time, as previously reported by Kumar *et al.* [21]. Although it has been previously reported that $[\text{Bmim}]\text{Br}$ can also produce metal-carbene complexes [54], the oxidation

generating a reactive *N*-heterocyclic carbene. This reactive species can serve as a ligand or ligand precursor for dissolving a transition metal complex [54]. Moreover, hydroxide ion is also used to regenerate reactive transition metal catalyst (see mechanism). Additionally, water can hydrate the hydroxide anion and prevent the formation of reactive carbene (Scheme 2) [56].

Table 3. Oxidation of α -hydroxy ketone **1a** and benzyl alcohol **3a** with KMnO_4 in recycled basic ionic liquid $[\text{Bmim}]\text{OH}$.

Cycle	Yield 2a (%) from substrate 1a	Yield 4a (%) from substrate 3a
1	90	91
2	88	89
3	85	86
4	83	84
5	80	81

process still needs higher reaction temperatures and longer reaction times. This is most likely because Br^- cannot function as a base during the regeneration of active metal-carbene complex, which needs base to abstract protons.



Scheme 3. A possible mechanism for formation products of **2a-l** and **4a-k** from substrate **1a-l** and **3a-k** oxidized by KMnO_4 in $[\text{Bmim}]\text{OH}$.

3. Material and Methods

All chemicals in the experiment were analytical grade and used directly without further purification, including some acyloin derivatives from our previous reports [9, 52-53]. The

melting points were determined in capillary tubes in a Buchi B 545 apparatus. The products were identified by comparing their melting points and spectral data (FTIR, ^1H & ^{13}C NMR) with those in the authentic samples. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury plus (400 MHz) spectrophotometer using TMS as internal standard and CDCl_3 as solvent and chemical shifts were expressed in ppm. Coupling constant (J) are reported in Hertz (Hz) and the multiplicity abbreviations used are singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The IR spectra were recorded using KBr pellets on a Shimadzu spectrometer which scans from 400 to 4000 wavenumber.

3.1 General Procedure for Selective Oxidation of α -Hydroxy Ketone Derivatives 1a-l to 1,2-Diarylethane-1,2-dione Derivatives 2a-l Using KMnO_4 in Basic Ionic Liquid of [Bmim]OH

In a round bottom flask, 1.0 mmol of α -hydroxy ketone compounds 1a-l were dissolved in 2.5 mL of [Bmim]OH, with stirring at room temperature and then 1.0 mmol of KMnO_4 was slowly added with stirring for 40-120 minute. After completion of the reaction (monitored by TLC, eluant: hexane/dichloromethane, 1:1), the product was extracted with diethyl ether (3 x 20 mL). The combined organic extract was dried (anh. Na_2SO_4), and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (silica gel, elution with hexane/dichloromethane, 1:1) and characterized by IR, ^1H and ^{13}C NMR spectroscopic data. The purified 1,2-diarylethane-1,2-dione products 2a-l with their physical data are listed below.

1,2-Diphenylethane-1,2-dione (2a): Yellow crystals, Yield 90%, mp 95-96 °C (lit. 95 °C) [57]; IR (KBr): ν_{max} 3064, 1660, 1594, 1450, 1325, 1211, 876 and 719 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.98 (4H, d, $J = 7.6$ Hz, 2-H, 6-H, 2'-H and 6'-H), 7.66 (2H, t, $J = 7.6$ Hz, 4-H and 4'-H) and 7.51 (4H, t, $J = 7.6$ Hz, 3-H, 5-H, 3'-H and 5'-H); ^{13}C NMR (CDCl_3): δ 129.0, 129.9, 133.0, 134.9 and 194.5

1,2-Di(4-chlorophenyl)ethane-1,2-dione (2b): Yellow crystals, Yield 94%, mp 197-198 °C (lit. 197-198 °C) [57]; IR (KBr): ν_{max} 3094, 2925, 1661, 1587, 1486, 1317, 1210 and 1094 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.91 (4H, d, $J = 8.4$ Hz, 2-H, 6-H, 2'-H and 6'-H) and 7.50 (4H, d, $J = 8.4$ Hz, 3-H, 5-H, 3'-H and 5'-H); ^{13}C NMR (CDCl_3): δ 129.5, 131.2, 131.3, 141.8 and 192.3

1,2-Di(4-methylphenyl)ethane-1,2-dione (2c): Yellow crystals, Yield 88%, mp 99-100 °C (lit. 103 °C) [58]; IR (KBr): ν_{max} 2922, 1667, 1604, 1573, 1440, 1410, 1321, 1220 and 1173 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.86 (4H, d, $J = 8.2$ Hz, 2-H, 6-H, 2'-H and 6'-H), 7.04 (4H, d, $J = 8.0$ Hz, 3-H, 5-H, 3'-H and 5'-H) and 2.43 (6H, s, 2(Ar- CH_3)); ^{13}C NMR (CDCl_3): δ 21.7, 126.5, 129.2, 130.2, 144.6 and 171.4

1,2-Di(4-methoxyphenyl)ethane-1,2-dione (2d): Yellow solid, Yield 85%, mp 132-134 °C (lit. 133 °C) [58]; IR (KBr): ν_{max} 3063, 2959, 2849, 1655, 1598, 1572, 1424, 1312, 1263 and 1161 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.95 (4H, d, $J = 8.8$ Hz, 2-H, 6-H, 2'-H and 6'-H), 6.97 (4H, d, $J = 8.8$ Hz, 3-H, 5-H, 3'-H and 5'-H) and 3.89 (6H, s, 2(Ar- OCH_3)); ^{13}C NMR (CDCl_3): δ 55.6, 114.3, 126.4, 132.4, 164.9 and 193.5

1,2-Di(4-fluorophenyl)ethane-1,2-dione (2e): Yellow crystals, Yield 96%, mp 120-122 °C (lit. 120-122 °C) [59]; IR (KBr): ν_{max} 3076, 2926, 2858, 1664, 1598, 1231, 1157 and 843 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.02 (4H, dd, $J = 8.8$ Hz and 5.2 Hz, 2-

H, 6-H, 2'-H and 6'-H) and 7.20 (4H, t, $J = 8.4$ Hz, 3-H, 5-H, 3'-H and 5'-H); ^{13}C NMR (CDCl_3): δ 116.5 (d, $J = 88.4$ Hz), 129.1 (d, $J = 234.8$ Hz), 132.8 (d, $J = 39.6$ Hz), 166.9 (d, $J = 1028.4$ Hz) and 192.2

1,2-Di-2-furanyl-1,2-ethanedione (2f): Yellow crystals, Yield 97%, mp 162-164 °C (lit. 165-166 °C) [60]; IR ν_{max} 3150, 3090, 1647, 1550, 1455, 1397, 1281, 1024 cm^{-1} ; ^1H NMR δ 7.78 (2H, s, 5- and 5'-H), 7.64 (2H, d, $J = 3.6$ Hz, 3- and 3'-H), 6.63 (2H, d, $J = 3.6$ Hz, 4- and 4'-H); ^{13}C NMR δ 113.1, 124.7, 149.4, 149.9, 185.3.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (2g): Yellow crystals, Yield 93%, mp 75-76 °C (lit. 75-76 °C) [61]; IR (KBr): ν_{max} 3092, 3065, 2924, 2854, 1668, 1587, 1449, 1320, 1209, 834 and 712 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.91 (2H, d, $J = 8.0$ Hz, 2-H and 6-H), 7.93 (2H, d, $J = 8.4$ Hz, 2'-H and 6'-H), 7.68 (1H, t, $J = 7.2$ Hz, 4'-H), 7.53 (2H, d, $J = 7.6$ Hz, 3-H and 5-H) and 7.50 (2H, d, $J = 8.4$ Hz, 3'-H and 5'-H); ^{13}C NMR (CDCl_3): δ 129.0, 129.4, 129.9, 131.2, 131.4, 132.8, 135.0, 141.6, 193.0 and 193.8

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (2h): Yellow liquid, Yield 89% [61]; IR (KBr): ν_{max} 3065, 3009, 2957, 2928, 2850, 1677, 1597, 1451, 1265, 1166, 1097, 1026 and 1167 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.96 (4H, t, $J = 8.4$ Hz, 2-H, 6-H, 2'-H and 6'-H), 7.65 (1H, t, $J = 7.6$ Hz, 4-H), 7.51 (2H, t, $J = 8.0$ Hz, 3-H and 5-H), 6.98 (2H, d, $J = 8.4$ Hz, 3'-H and 5'-H) and 3.89 (3H, s, Ar- OCH_3); ^{13}C NMR (CDCl_3): δ 55.6, 114.4, 126.1, 128.9, 129.9, 132.4, 133.2, 134.7, 165.0, 193.1 and 194.8

1-(4-Chlorophenyl)-2-p-tolyethane-1,2-dione (2i): Yellow liquid, Yield 92% [62]; IR (neat): ν_{max} 3093, 3065, 2924, 2856, 1663, 1585, 1484, 1315, 1211, 1171, 1091, 831 and 736 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.92 (2H, d, $J = 8.4$ Hz, 2'-H and 6'-H), 7.86 (2H, d, $J = 8.0$ Hz, 2-H and 6-H), 7.48 (2H, d, $J = 8.4$ Hz, 3'-H and 5'-H), 7.31 (2H, d, $J = 7.6$ Hz, 3-H and 5-H) and 2.44 (3H, s, Ar- CH_3); ^{13}C NMR (CDCl_3): δ 21.9, 129.4, 129.8, 130.0, 130.4, 131.2, 131.5, 141.4, 146.4, 193.2 and 193.5

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-ethane-1,2-dione (2j): Yellow liquid, Yield 91% [62]; IR (neat): ν_{max} 3095, 2968, 2924, 1666, 1572, 1510, 1487, 1313, 1265, 1167, 1094, 879 and 743 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.94 (2H, d, $J = 8.4$ Hz, 2'-H and 6'-H), 7.92 (2H, d, $J = 8.0$ Hz, 2-H and 6-H), 7.48 (2H, d, $J = 8.4$ Hz, 3'-H and 5'-H), 6.98 (2H, d, $J = 8.8$ Hz, 3-H and 5-H) and 3.89 (3H, s, Ar- OCH_3); ^{13}C NMR (CDCl_3): δ 55.6, 114.4, 125.9, 129.3, 131.2, 131.6, 132.4, 141.3, 165.1, 192.4 and 193.3

1-(4-Methoxyphenyl)-2-p-tolyethane-1,2-dione (2k): Yellow liquid, Yield 87% [62]; IR (neat): ν_{max} 2929, 2850, 1666, 1596, 1510, 1456, 1309, 1260 and 1024 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.94 (2H, d, $J = 8.8$ Hz, 2-H and 6-H), 7.86 (2H, d, $J = 8.0$ Hz, 2'-H and 6'-H), 7.30 (2H, d, $J = 8.0$ Hz, 3'-H and 5'-H), 6.97 (2H, d, $J = 8.8$ Hz, 3-H and 5-H), 3.88 (3H, s, Ar- OCH_3) and 2.43 (3H, s, Ar- CH_3); ^{13}C NMR (CDCl_3): δ 21.9, 55.6, 114.3, 126.2, 129.6, 130.0, 130.8, 132.3, 145.9, 164.9, 193.3 and 194.6

1-(4-Chlorophenyl)-2-(4-nitrophenyl)-ethane-1,2-dione (2l): Yellow crystals, Yield 95%, mp 191-192 °C (lit. 192 °C) [63]; IR (KBr): ν_{max} 2957, 2924, 1724, 1596, 1523, 1457, 1349, 1266, 1090, 842 and 756 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.26 (2H, d, $J = 8.8$ Hz, 3'-H and 5'-H), 8.02 (2H, d, $J = 8.4$ Hz, 2'-H and 6'-H), 7.60 (2H, d, $J = 8.8$ Hz, 2-H and 6-H) and 7.45 (2H, d, $J = 8.4$ Hz, 3-H and 5-H); ^{13}C NMR (CDCl_3): δ 123.9, 127.9, 128.4, 128.9, 131.1, 140.0, 143.0, 165.2, 193.4 and 193.9

3.2 General Procedure for Selective Oxidation of Alcohols 3a-

I to Aldehydes and Ketones 4a-l Using KMnO₄ in Basic Ionic Liquid of [Bmim]OH

A mixture of alcohols 1.0 mmol (primary or secondary alcohols) and [Bmim]OH 2.5 mL was stirred at room temperature, and then 1.0 mmol of KMnO₄ was slowly added for 30-55 minutes. After completion of the reaction (monitored by TLC, eluant: hexane/ethyl acetate, 1:1), the product was extracted with diethyl ether (3 X 20 mL). The crude extract was dried (anh. Na₂SO₄), and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (silica gel, elution with hexane/ethyl acetate, 1:1) to give expected products (aldehydes **4a-g** or ketone **4h-k**) was characterized by ¹H and ¹³C NMR spectroscopic data. The purified aldehydes **4a-g** and ketones products **4a-g** with their physical data are listed below.

Benzaldehyde (4a): Colorless liquid, Yield 91% [21]; ¹H NMR (CDCl₃) δ 10.20 (1H, s, C₆H₅CHO), 8.06 (2H, d, J = 8.4 Hz, 2-H and 6-H), 7.81 (1H, t, J = 7.6 Hz, 4-H), 7.71 (2H, t, J = 7.8 Hz, 3-H and 5-H); ¹³C NMR (CDCl₃) δ 129.0, 129.8, 134.5, 136.4, 192.4,

4-Chlorobenzaldehyde (4b): Colorless crystal, Yield 93%, mp 45-47 °C (lit. 47 °C) [21]; ¹H NMR (CDCl₃) δ 10.01 (1H, s, 4-ClC₆H₄CHO), 7.85 (2H, d, J = 8.4 Hz, 2-H and 6-H), 7.54 (2H, d, J = 8.4 Hz, 3-H and 5-H); ¹³C NMR (CDCl₃) δ 129.5, 130.9, 134.8, 141.0, 191.0,

4-Bromobenzaldehyde (4c): Yellow liquid, Yield 95% [64]; ¹H NMR (CDCl₃) δ 10.14 (1H, s, 4-BrC₆H₄CHO), 7.91 (2H, d, J = 8.8 Hz, 2-H and 6-H), 7.85 (2H, d, J = 8.4 Hz, 3-H and 5-H); ¹³C NMR (CDCl₃) δ 129.8, 131.0, 132.5, 135.1, 191.1

p-Tolualdehyde (4d): Pale yellow liquid, Yield 89% [64]; ¹H NMR (CDCl₃) δ 9.93 (1H, s, 4-CH₃C₆H₄CHO), 7.76–7.73 (2H, m, 2-H and 6-H), 7.30 (2H, d, J = 8.0 Hz, 3-H and 5-H), 2.40 (3H, s, CH₃); ¹³C NMR (CDCl₃) δ 21.8, 129.6, 129.8, 134.2, 145.6, 192.0

4-Methoxybenzaldehyde (4e): Yellow liquid, Yield 87% [21]; ¹H NMR (CDCl₃) δ 9.81 (1H, s, 4-CH₃OC₆H₄CHO), 7.80–7.74 (2H, m, 2-H and 6-H), 6.96–6.91 (2H, m, 3-H and 5-H), 3.81 (3H, s, OCH₃); ¹³C NMR (CDCl₃) δ 55.6, 114.3, 130.0, 132.0, 164.7, 190.9

4-Fluorobenzaldehyde (4f): Yellow liquid, Yield 97% [64]; ¹H NMR (CDCl₃) δ 9.97 (1H, s, 4-FC₆H₄CHO), 7.91 (2H, dd, J = 8.8 Hz and 5.2 Hz, 2-H and 6-H), 7.21 (2H, t, J = 8.4 Hz, 3-H and 5-H); ¹³C NMR (CDCl₃) δ 116.3 (d, J = 22.2 Hz), 132.2 (d, J = 10.1 Hz), 133.0, 166.5 (d, J = 255.2 Hz), 190.5

2-Hydroxybenzaldehyde (4g): Colorless clarifying oily liquid, Yield 88% [64]; ¹H NMR (CDCl₃) δ 11.04 (1H, s, OH), 9.90 (1H, s, 2-OHC₆H₄CHO), 7.58–7.52 (2H, m, 4-H and 6-H), 7.05–6.99 (2H, m, 3-H and 5-H); ¹³C NMR (CDCl₃) δ 117.6, 120.3, 133.8, 137.0, 161.7, 196.6

Acetophenone (4h): Colorless liquid, Yield 85%, [65]; ¹H NMR (CDCl₃) δ 7.95 (2H, d, J = 8.4 Hz, 2-H and 6-H), 7.65–7.59 (1H, m, 4-H), 7.53–7.48 (2H, m, 3-H and 5-H), 2.57 (3H, s, COCH₃); ¹³C NMR (CDCl₃) δ 27.3, 128.8, 129.3, 133.8, 137.5, 198.5

4-Chloroacetophenone (4i): White liquid, Yield 87% [65]; ¹H NMR (CDCl₃) δ 7.96 (2H, d, J = 8.4 Hz, 2-H and 6-H), 7.57 (2H, d, J = 8.4 Hz, 3-H and 5-H), 2.58 (3H, s, COCH₃); ¹³C NMR (CDCl₃) δ 27.2, 129.2, 130.5, 136.0, 138.6, 197.3

4-Nitroacetophenone (4j): Yellow solid, Yield 86%, mp 104-106 °C (lit. 106 °C) [21]; ¹H NMR (CDCl₃) δ 8.34 (2H, d, J = 8.4 Hz, 2-H and 6-H), 8.13 (2H, d, J = 8.4 Hz, 3-H and 5-H), 2.70

(3H, s, COCH₃); ¹³C NMR (CDCl₃) δ 27.0, 123.9, 129.3, 141.4, 150.4, 196.3

Benzophenone (4k): Colorless crystal, Yield 83%, mp 47 °C [64]; ¹H NMR (CDCl₃) δ 7.83 (4H, d, J = 8.4 Hz, 2-H, 6-H, 2'-H and 6'-H), 7.62 (2H, t, J = 7.4 Hz, 4-H and 4'-H), 7.51 (4H, t, J = 7.6 Hz, 3-H, 5-H, 3'-H and 5'-H); ¹³C NMR (CDCl₃) δ 128.3, 130.1, 132.5, 137.6, 176.4

4. Conclusions

In conclusion, we developed a greener method for the synthesis of 1,2-diarylethane-1,2-dione as well as aldehyde and ketone derivatives by the oxidative agent (KMnO₄) under basic ionic liquid media [Bmim]OH at room temperature. These reactions are mild, fast, and efficient for selective oxidation of α-hydroxy ketones derivatives and some alcohols lead to corresponding carbonyl compounds (**2a-l** and **4a-k**) in high yields (85-97% and 83-97%, respectively). The recovered KMnO₄ in [Bmim]OH after the extraction can be reused four times without significant loss of efficiency, which is of paramount importance for both economic and environmental reasons.

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Author Contributions

Pakin Noppawan and Kanokkan Worawut participated in data analysis and drafted manuscript. Baramee Phungpis conceived the study, designed the study, coordinated the study, carried out data analysis, interpreted the results and aided in drafting the manuscript. All authors gave final approval for publication.

References and Notes

- [1] Freemantle, M. *Chem. Eng. News* **1998**, *76*, 32. [\[Crossref\]](#)
- [2] Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221. [\[Crossref\]](#)
- [3] Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459. [\[Crossref\]](#)
- [4] Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667. [\[Crossref\]](#)
- [5] Ranu, B. C.; Banerjee, S. *Org. Lett.* **2005**, *7*, 3049. [\[Crossref\]](#)
- [6] Ranu, B. C.; Jana, R. *Eur. J. Org. Chem.* **2006**, *2006*, 3767. [\[Crossref\]](#)
- [7] Nguyen, T. T. D.; Tran, H. P. *VJSTE.* **2018**, *60*, 3. [\[Crossref\]](#)
- [8] Xu, J.-M.; Liu, B.-K.; Wu, W.-B.; Qian, C.; Wu, Q.; Lin, X.-F. *J. Org. Chem.* **2006**, *71*, 3991. [\[Crossref\]](#)
- [9] Phungpis, B.; Hahnvajanawong, V.; Theramongkol, P. *Orient. J. Chem.* **2014**, *30*, 933. [\[Crossref\]](#)
- [10] Kumari, C.; Goswami, A. *Eur. J. Org. Chem.* **2021**, *2021*, 429. [\[Crossref\]](#)

- [11] Vishal S.; Pravin K. S.; Surabhi S.; Praveen P. S. *Rev. Roum. Chim.* **2016**, *61*, 755.
- [12] Zang, H.; Wang, M.; Cheng, B. -W.; Song, J. *Ultrason. Sonochem.* **2009**, *16*, 301. [\[Crossref\]](#)
- [13] Padvi, S. A.; Tayade, Y. A.; Wagh, Y. B.; Dalal, D. S. *Chin. Chem. Lett.* **2016**, *27*, 714. [\[Crossref\]](#)
- [14] Comprehensive Organic Synthesis. Trost, B. M.; Fleming, I., eds. Oxford: Pergamon Press, 1991, Volume 7.
- [15] Hudlick, M. Oxidations in Organic Chemistry, Washington, D.C.: American Chemical Society, 1990.
- [16] Sheldon, R. A.; Kochi, J. K. Metal Catalyzed Oxidations of Organic Compounds, New York: Academic Press, 1981, chapter 6.
- [17] Li, M.; Klunder, K.; Blumenthal, E.; Prater, M. B.; Lee, J.; Matthiesen, J. E.; Minter, S. D. *ACS Sustainable Chem. Eng.* **2020**, *8*, 4489. [\[Crossref\]](#)
- [18] Souza, R. F.; Dupont, J.; Dullius, J. E. de L. *J. Braz. Chem. Soc.* **2006**, *17*, 48. [\[Crossref\]](#)
- [19] Qian, W.; Jin, E.; Bao, W.; Zhang, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 952. [\[Crossref\]](#)
- [20] Zheng, Y.-F.; Du, X.-F.; Bao, W.-L. *J. Chem. Res.* **2005**, *2005*, 753. [\[Crossref\]](#)
- [21] Kumar, A.; Jain, N.; Chauhan, S. M. S. *Synth. Commun.* **2004**, *34*, 2835. [\[Crossref\]](#)
- [22] Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037. [\[Crossref\]](#)
- [23] Ebitani, K.; Ji, H.-B.; Mizugaki, T.; Kaneda, K. *J Mol Catal A Chem.* **2004**, *212*, 161. [\[Crossref\]](#)
- [24] Makwana, V. D.; Son, Y.-C.; Howell, A. R.; Suib, S. L. *J. Catal.* **2002**, *210*, 46. [\[Crossref\]](#)
- [25] Kobayashi, S.; Miyamura, H.; Akiyama, R.; Ishid, T.; *J. Am. Chem. Soc.* **2005**, *127*, 9251. [\[Crossref\]](#)
- [26] Ferri, D.; Mondelli, C.; Krumeich, F.; Baiker, A. *J. Phys. Chem. B.* **2006**, *110*, 22982. [\[Crossref\]](#)
- [27] Jensen, D. R.; Sigman, M. S.; *Org. Lett.* **2003**, *5*, 63. [\[Crossref\]](#)
- [28] Baragwanath, L.; Rose, C. A.; Zeitler, K.; Connon, S. J. *J. Org. Chem.* **2009**, *74*, 9214. [\[Crossref\]](#)
- [29] Knight, R. L.; Leeper, F. J. *J. Chem. Soc. Perkin Trans. I.* **1998**, 1891. [\[Crossref\]](#)
- [30] Rose, C. A.; Gundala, S.; Connon, S. J.; Zeitler, K. *Synthesis.* **2011**, 0190. [\[Crossref\]](#)
- [31] Kuhl, N.; Glorius, F. *Chem. Commun.* **2011**, *47*, 573. [\[Crossref\]](#)
- [32] Rose, C. A.; Gundala, S.; Fagan, C.-L.; Franz, J. F.; Connon, S. J.; Zeitler, K. *Chem. Sci.* **2012**, *3*, 735. [\[Crossref\]](#)
- [33] Enders, D.; Henseler, A. *Adv. Synth. Catal.* **2009**, *351*, 1749. [\[Crossref\]](#)
- [34] Ma, B.-Q.; Vieira Ferreira, L. F.; Coppens, P. *Org. Lett.* **2004**, *6*, 1087. [\[Crossref\]](#)
- [35] Zheng, S.-L.; Coppens, P. *CrystEngComm.* **2005**, *7*, 289. [\[Crossref\]](#)
- [36] Prasad, G.; Giri, B. P.; Mehrotra, K. N. *J. Org. Chem.* **1982**, *47*, 2353. [\[Crossref\]](#)
- [37] Hatanaka, M.; Nishizawa, C.; Kakinoki, T.; Takahashi, K.; Nakamura, S.; Mashino, T. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5290. [\[Crossref\]](#)
- [38] Hatanaka, M.; Takahashi, K.; Nakamura, S.; Mashino, T. *Bioorg. Med. Chem.* **2005**, *13*, 6763. [\[Crossref\]](#)
- [39] Giraud, A.; Provot, O.; Peyrat, J.-F.; Alami, M.; Brion, J.-D. *Tetrahedron.* **2006**, *62*, 7667. [\[Crossref\]](#)
- [40] Ogata, Y.; Kawasaki, A.; Sugiura, F. *J. Org. Chem.* **1969**, *34*, 3981. [\[Crossref\]](#)
- [41] Prasad, G.; Giri, B. P.; Mehrotra, K. N. *J. Org. Chem.* **1982**, *47*, 2353. [\[Crossref\]](#)
- [42] Marjani, K.; Asgarian, J.; Mousavi, M. *J. Chem. Res.* **2007**, *9*, 548. [\[Crossref\]](#)
- [43] Marjani, K.; Moghadam, M. S.; Arazi, O.; Mousavi, M. *Acta Cryst. E.* **2007**, *E63*, o3519. [\[Crossref\]](#)
- [44] Marjani, K.; Mousavi, M.; Ashouri, A.; Arazi, O.; Bourghani, S.; Asgari, M. *J. Chem. Res.* **2008**, 398. [\[Crossref\]](#)
- [45] Marjani, K.; Mousavi, M.; Arazi, O.; Ashouri, A.; Bourghani, S.; Rajabi, M. *Monatshefte fuer Chemie.* **2009**, *140*, 1331. [\[Crossref\]](#)
- [46] Sanniccolo, F. *J. Org. Chem.* **1983**, *48*, 2924. [\[Crossref\]](#)
- [47] Coan, S. B.; Trucker, D. E.; Beckerr, E. I. *J. Am. Chem. Soc.* **1955**, *77*, 60. [\[Crossref\]](#)
- [48] Maly, K. E.; Gagnon, E.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 4306. [\[Crossref\]](#)
- [49] Arquero, A.; Cañadas, M.; Martinez-Ripoll, M.; Antonia Mendiola, M.; Rodriguez, A. *Tetrahedron* **1998**, *54*, 11271. [\[Crossref\]](#)
- [50] Jones, L. A.; Hancock, C. K.; Seligman, R. B. *J. Org. Chem.* **1961**, *26*, 228. [\[Crossref\]](#)
- [51] Raman, N.; Ravichandran, S.; Thangaraja, C. *J. Chem. Sci.* **2004**, *116*, 215. [\[Crossref\]](#)
- [52] Hahnvajanawong, V.; Waengdongbung, W.; Piekkaew, S.; Phungpis, B.; Theramongkol, P. *ScienceAsia* **2013**, *39*, 50. [\[Crossref\]](#)
- [53] Phungpis, B.; Worawut, K.; Keawkumsan, P. *ASEAN J. Sci. Tech. Report.* **2021**, *24*, 91. [\[Crossref\]](#)
- [54] Safaei-Ghomi, J.; Hajipour, A. R.; Esmaili, M. *Dig. J. Nanomater. Bios.* **2010**, *5*, 865.
- [55] Shaabani, A.; Tavasoli-Rad, F.; Lee, D. G. *Synth. Commun.* **2005**, *35*, 571. [\[Crossref\]](#)
- [56] Yuen, A. K. L.; Masters, A. F.; Maschmeyer, T. *Catal. Today* **2013**, *200*, 9. [\[Crossref\]](#)
- [57] Buckingham, J. Dictionary of Organic Compounds, 5th ed. New York: Chapman and Hall/CRC, 1982.
- [58] Pouchert, C. J.; Behnke, J. The Aldrich Library of NMR Spectra. Wisconsin: Milwaukee, 1991, Volume 2.
- [59] Ponomarev, I. I.; Razorenov, D. Y.; Petrovskii, P. V. *Russ. Chem. Bull.* **2009**, *58*, 2376. [\[Crossref\]](#)
- [60] Wang, L. Y.; Meng, D.; Li, L.; Cai, X. *Advanced Materials Research.* **2012**, *554*, 764. [\[Crossref\]](#)
- [61] Suzuki, H.; Ninomiya, K.; Inouye, M. *Chem. Lett.* **1985**, *14*, 821. [\[Crossref\]](#)
- [62] Phungpis, B.; Hahnvajanawong, V. *Asian J. Chem.* **2021**, *33*, 651. [\[Crossref\]](#)
- [63] Chen, M.; Zhao, Q.; She, D.-B.; Yang, M.-Y.; Hui, H.-H.; Huang, G.-S. *J. Chem. Sci.* **2008**, *120*, 347. [\[Crossref\]](#)
- [64] Zhang, M.; Zhai, Y.; Ru, S.; Zang, D.; Han, S.; Yu, H.; Wei, Y. *Chem. Commun.* **2018**, *54*, 10164. [\[Crossref\]](#)
- [65] Rong, M.; Liu, C.; Han, J.; Sheng, W.; Zhang, Y.; Wang, H. *Catal. Lett.* **2008**, *125*, 52. [\[Crossref\]](#)

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