

Research Article

An Efficient Oxidation of Benzoin to Benzil by Manganese(II) Schiff Base Complexes Using Green Oxidant

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A simple, highly efficient and mild catalytic oxidation of benzoin to the corresponding benzil was developed using manganese(II) Schiff base complexes as novel and reusable catalyst in the presence of acetonitrile as solvent and H_2O_2 as green oxidant. This simple method affords benzil derivatives at room temperature in short reaction times with high yield and purity. This convenient procedure will allow a further increase of the diversity within the benzil family.

1. Introduction

Benzil, an alpha diketone, is one of the important organic intermediates and has received an enormous attention because of its practical applications in organic and pharmaceutical industry such as photosensitive and synthetic reagents [1–3]. The oxidation of benzoin is one of the most efficient and practical methods for the synthesis of benzils. In general, the oxidation of benzoin to benzils has been accomplished by classical reagents such as nitric acid [4], Fehling's solution [4], thallium nitrate [5], ammonium nitrate—copper acetate [6], bismuth nitrate—copper acetate [7], and ferric nitrate [8]. In addition, the oxidation of benzoin to benzils was studied using *p*-benzoquinone or air in the presence of $(\text{Fe}^{\text{II}}(\text{SPh})_4)_2$ and $(\text{Fe}^{\text{II}}(\text{SePh})_4)_2$ [9], Fe(II)-cysteine peptide complexes [7] and *tert*-butyl peroxide [10]. The electrochemical oxidation of benzoin to benzils in the presence of a catalytic amount of KI in basic media [11] was also studied. Also, Paris et al. used $(\text{Mn}^{\text{III}}(\text{pydx-en})\text{Cl}(\text{H}_2\text{O}))\cdot\text{Y}$ as catalyst and H_2O_2 as an oxidant for oxidation of benzoin to benzil in methanol at reflux temperature [12].

However, in spite of their potential utility, some of the reported methods suffer from drawbacks such as longer reaction time, lower yields, expensive catalysts, harsh conditions,

or complexity of workup. There still appears a need either to improve the existing oxidation methods or to introduce novel reagents to permit better selectivity under milder conditions and with easy work-up procedures [12].

Transition metal catalysts supported by Schiff base ligands have assumed a prominent role in modern synthesis. Schiff base complexes of transition metals having O and N donor atoms have shown an exponential increase as inorganic catalysts for various organic transformations. Distinct advantages of such ligands include their low cost, facile syntheses, and convenient incorporation of inexpensive, chiral 1,2-diamines into the ligand backbone. Moreover, the ligands generally afford air and moisture-stable complexes. On the other hand, coordination chemistry of manganese has been studied extensively so that that manganese center is surrounded by O- or N-donor ligands [13, 14]. In addition, they also act as catalysts for important reactions [15–20].

The development of manganese(II) Schiff base heterogeneous catalysts for oxidation reaction has become a major area of research recently [21–23], as the potential advantages of these materials over homogeneous systems can make a major impact on the environmental performance of a synthesis. While the homogeneous catalysts exhibit excellent activity and selectivity, the technical problems encountered

in their use, such as the difficulty in product separation, long reaction times, self-aggregation of active sites, and undesirable side products [24]. In order to overcome the problems associated with homogeneous systems, heterogeneous catalyst was used in Organic Chemistry. In the present study, we have reported a simple and convenient method for the effective oxidation of benzoin derivatives to corresponding benzils under mild conditions by manganese(II) Schiff base complex and H_2O_2 at room temperature (Scheme 1). H_2O_2 is inexpensive and environmental friendly oxidant. It is observed that the homogeneous catalyst is very active in high conversion rate of benzoin to benzil. However, the homogeneous catalysts have the difficulty in separating the catalysts from the reaction mixture at the end of the process. But, this simple method aimed to overcome the limitations. The easy removal of the catalyst makes them better compared to other homogeneous catalyst. Moreover, the catalytic oxidation can be carried out at room temperature in short reaction time with high yield and purity.

2. Experimental

2.1. Materials. Chemicals were purchased from the Merck and Fluka Chemical Companies in high purity. All of the materials were of commercial reagent grade. The amines and carbonyl compounds were purified by standard procedures [25].

2.2. Apparatus. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and on an Impact 400 Nicolet FTIR spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX-400 Avance spectrometer. Tetramethyl silane (TMS) was used as an internal reference. UV spectra were recorded on a Hitachi 200-20 spectrometer using spectrophotometric grade ethanol (Baker). The melting points were determined by a Yanagimoto micromelting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica gel polygram SILG/UV 254 plates.

2.3. General Procedure

2.3.1. General Procedure for the Preparation of the Schiff Base Ligands. To a mixture of salicylaldehyde (0.4 g, 3.27 mmol) in MeOH was added the diamine (1.65 mmol) with stirring in one portion. The stirring was continued to complete the reaction. The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, a colored substance was obtained. The solid product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization from ethanol and the pure Schiff base was obtained in high yield after leaving for the appropriate time. The Schiff base products were identified by physical and spectroscopic data and by a comparison with authentic samples prepared in accordance to the literature procedures (Scheme 2) [26].

N,N'-Bis(salicylidene)ethylenediamin (Salen): Yellow. Yield: 93%; M.P: 125–127°C. ^1H NMR (CDCl_3 , 400 MHz) δ : 3.96 (s, 4H), 6.88 (t, 2H, Ar), 6.95 (t, 2H, Ar), 7.20 (q, 2H, Ar), 7.28 (q, 2H, Ar), 8.23 (s, 2CH), 13.23 (s, 2OH) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ : 57.41, 117.32, 118.91, 121.62, 130.39, 132.31, 158.33, 161.19; IR (KBr, ν_{max} , cm^{-1}): 3250–3550, 1634, 1416, 1570, 1285.

2.3.2. General Procedure for the Preparation of the Schiff Base Complexes of Mn(II). To a solution of the Schiff base ligand (1 mmol) in MeOH (10 mL) was added $\text{Mn}(\text{O}_2\text{CCH}_3)_2$ (1 mmol) dropwise under refluxing conditions. The reaction mixture was stirred to complete the reaction. The progress of the reaction was monitored by TLC. After the completion of complex formation, a colored substance was obtained. The solid product was filtered off and washed with MeOH. The crude product was purified by recrystallization from methanol and the pure Schiff base complex was obtained. The complex products were identified by comparison with authentic samples prepared in accordance to the literature procedures (Scheme 2) [26].

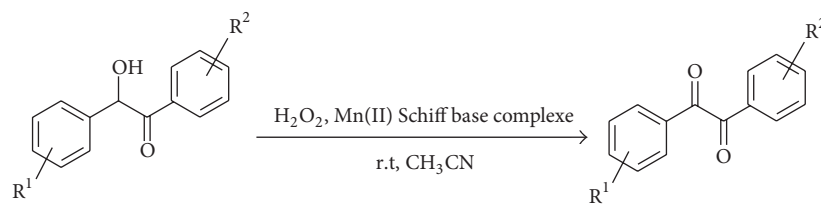
N,N'-Bis(salicylidene)ethylenediaminemanganese(II) (Mn (Salen)): Dark green. Yield: 88%; M.P.: >300°C. ^1H NMR (CDCl_3 , 400 MHz) δ : 4.3 (s (br), 4H), 6.35 (t, 2H, Ar), 7.24 (t, 2H, Ar), 7.41 (q, 2H, Ar), 7.39 (q, 2H, Ar), 8.71 (s (br), 2CH), ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ : 57.41, 117.32, 118.91, 121.62, 130.39, 132.31, 158.33, 161.19; IR (KBr, ν_{max} , cm^{-1}): 1621, 1402, 1568, 1283.

2.3.3. General Procedure for Oxidation of Benzoin to Benzil. Oxidation of benzoin was carried out using Mn(II) Schiff base complexes as a catalyst in a 50 mL flask. In a typical reaction, 1 mmol of benzoin was dissolved in 10 mL acetonitrile in the presence of KOH. Oxidation of reaction mixture was done with H_2O_2 with catalytic amount manganese(II) Schiff base. The reaction mixture was stirred to completion at room temperature and gave excellent yields under the mild oxidation conditions. The completion of reaction was monitored by TLC (petroleum ether: ethyl acetate, 4:1 v/v). After the completion of the reaction, the catalyst was removed by addition of absolute methanol to the mixture and Schiff base complex was recrystallized from petroleum ether. The solvent was evaporated, and the pure benzil derivatives were obtained. The structure of these compounds has been investigated using different methods of spectroscopy and spectrometry: UV, ^1H NMR, ^{13}C NMR, IR, and MS.

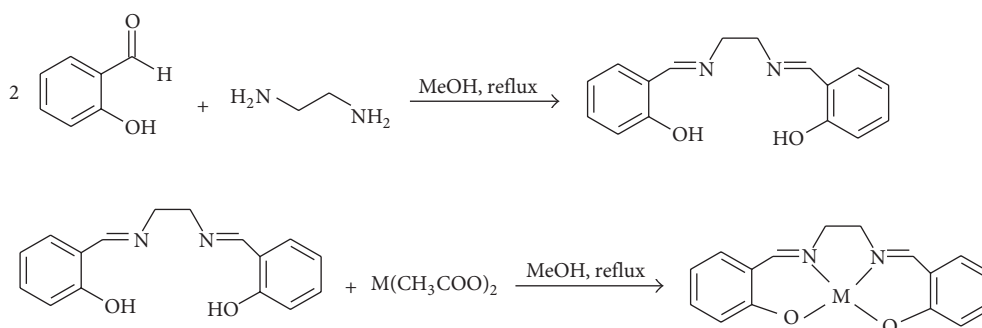
3. Results and Discussion

Schiff base complexes of metal(II) have been recognized as being among the most promising catalysts for various reactions. We used Mn(II) Schiff base complexes as catalyst and H_2O_2 as oxidant, for the oxidation of some benzoin into benzils at room temperature in high yield.

Firstly, among the various oxidants, it was concluded that the best activity and selectivity can be achieved by H_2O_2 under optimized reaction conditions. Diluted solution



SCHEME 1: Oxidation of symmetrical and unsymmetrical benzoin derivatives to benzil derivatives using H_2O_2 and manganese(II) Schiff base complex.



SCHEME 2: Preparation of the Schiff base complexes of metal(II) as catalyst.

of hydrogen peroxide is a universal, ecologically clean and convenient way to handle reagents for different oxidations in the liquid phase [27, 28]. This is an environmentally friendly oxidizing agent as its breakdown products are water and oxygen. Therefore, its decomposition produces no other pollutant in the environment. As shown in Table 1, the effect of Oxidant on the reaction was studied by considering substrate-to-oxidant ratios of 1:1, 1:1.5, 1:2, 1:2.5, and 1:3 for the substrate (0.2 g, 1 mmol) in 10 mL of CH_3CN at room temperature. The yield increases from 52% to 98% with increasing substrate-to-oxidant ratios from 1:1 to 1:2. At the substrate to oxidant ratio of 1:2, the best yield of benzil was achieved (Table 1, Entry 3). Experiments under the same conditions in the absence of catalyst were also performed and only small amounts of product were detected in the reaction mixture.

We initiated a solvent screen to explore the effect of different solvents on the oxidation of benzoin and also summarized in Table 2. The results in Table 2 show that the highest yield of benzil was achieved with acetonitrile. When other solvents were used, no significant improvement in the yield was observed. In the oxidation procedure, acetonitrile was chosen because of its high polarity and solubility of catalyst in the solvent.

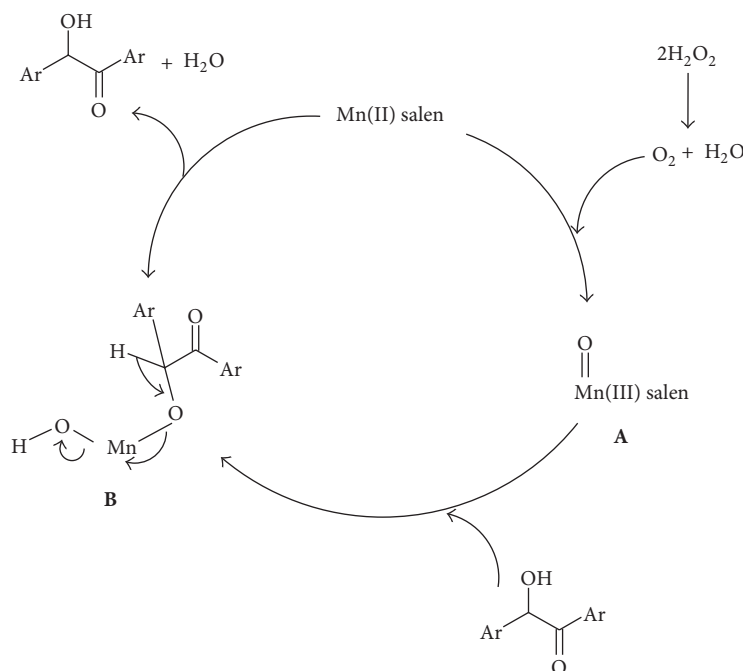
After the completion of the reaction, the catalyst was removed by addition of absolute methanol to the mixture and Schiff base complex was recrystallized from petroleum ether. Then the solvent was removed by evaporation under reduced pressure to give the pure products. Under this

condition, several benzoin derivatives were oxidized to the corresponding benzils. The results are summarized in Table 3. Oxidation of the benzoin substrates proceeded with decomposition of hydrogen peroxide in the presence of the Schiff base complex catalyst at room temperature. The results clearly suggest that Mn(II) Schiff base complex efficiently catalyses the conversion of benzoin to benzil in CH_3CN . The greater activity of the $(\text{OH})_2$ -salen system has clearly arisen from the existence of an electron donating ligand which facilitates the electron transfer rate, a process that has previously been observed in other oxidation reactions [29–34]. A cyclic mechanism has been proposed for the oxidation of benzoin using catalyst Mn(II) Schiff base complex with hydrogen peroxide as an oxidant (Scheme 3). An oxygen molecule from decomposition of H_2O_2 reacts with Mn(II) to form an oxomanganese complex A [35, 36], which undergoes oxidative addition to benzoin and gives an intermediate B which finally undergoes reductive elimination to give the desired product [37] and Mn(II) is regenerated back.

As shown in Table 3, the oxidation of benzoin by Mn(II) Schiff base complex was carried out in good yield at room temperature. From the results in Table 3, it seems that the benzoin containing electron-donating group were found to be more reactive and could be oxidized more easily (b and f). In contrast, the benzoin containing electron-withdrawing group have shown lower reactivity (j). This shows that the electronic effects of substituents have a significant role in the oxidation.

TABLE 1: The effect of reaction conditions on the oxidation of benzoin in the presence of Mn(II) Schiff base complex in CH₃CN at room temperature.

Entry	Molar ratio	Time	Schiff base complex (mmol)	Isolated yield (%)
1	1 : 1	25	0.01	52
2	1 : 1.5	25	0.01	68
3	1 : 2	25	0.01	98
4	1 : 2.5	25	0.01	82
5	1 : 3	25	0.01	75



SCHEME 3: Proposed catalytic cycle for the oxidation of benzoin to benzil using catalyst Mn(II) Schiff base complex with hydrogen peroxide as an oxidant.

TABLE 2: The effect of solvent on the yield of reaction at room temperature.

Solvent	Unreacted benzoin (%)	Yield (%) ^a
CH ₃ CN	2	98
CCl ₄	40	60
CH ₂ Cl ₂	70	30
CH ₃ OH	—	—
CH ₃ CH ₂ OH	—	—

^a Yields refer to the pure isolated product.

After completion of reaction, the catalyst was washed with petroleum ether (3 times) and then kept for drying at 100°C for 2 h, after which the catalyst was reused for next cycle without any appreciable loss of its activity. Similarly, reusability for sequential reaction was also carried out and catalyst was found to be reusable for five cycles (Table 4).

Finally, the structure of these compounds has been investigated using different methods of spectroscopy and spectrometry: UV, ¹H NMR, ¹³C NMR, IR, and MS.

4. Spectroscopic Data

Compound (a) Benzil: UV (CH₃OH) λ_{max}: 224 nm; ¹H NMR (CDCl₃, 400 MHz) δ: 7.54 (t, 2H, CH, J = 7.6 Hz), 7.69 (t, 4H, CH, J = 7.6 Hz), 7.98 (d, 4H, CH, J = 7.6 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ: 128.90 (4CH), 129.70 (4CH), 133 (2CH), 134.93 (2C), 194.30 (2CO) ppm; IR (KBr, ν_{max}, cm⁻¹): 1650 (C=O, s), 1450, 1580 (C=C, m), 720 (CH, m); MS (70 Ev, EI) m/z = 208 (M⁺), 104, 76.

Compound (b), 4,4'-dimethoxybenzil: UV (CH₃OH) λ_{max}: 225 nm; ¹H NMR (CDCl₃, 400 MHz) δ: 3.89 (s, 6H, OCH₃), 6.97 (d, 4H, CH, J = 8.8 Hz), 7.95 (d, 4H, CH, J = 8.8 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ: 55.62 (2OCH₃), 114.29 (4CH), 126.19 (4CH), 132.30 (2C), 64.86 (2C), 193.54

TABLE 3: Oxidation of benzoin derivatives using H₂O₂ in the presence of Mn(II) Schiff base complex in CH₃CN at room temperature.

	R ¹	R ²	Time (min)	Yield ^a (%)	mp _{rep} /mp _{lit.} (°C)
a	H	H	25	98	92–95/94–96 [24]
b	4-OCH ₃	4-OCH ₃	20	91	133–135/132–134 [24]
c	4-NCH ₃	H	30	70	117–118/115–116 [24]
d	4-CH ₃	4-CH ₃	23	78	103–105/101–104 [24]
e	4-OCH ₃	H	20	85	65–67/62–63 [24]
f	NC ₅ H ₅	NC ₅ H ₅	22	89	119–121
g	2,4-diOCH ₃	2,4-diOCH ₃	35	73	195–197
h	H	3-OCH ₃	21	58	133–134/133 [24]
i	H	4-CH ₃	26	84	27–28/31 [24]
j	4-CH ₃	3-Br	30	45	141–142

^a Isolated yields.

TABLE 4: Reusability study of Mn(II) Schiff base complex as catalyst for oxidation of benzoin.

Run	Yield (%)
1	98
2	95
3	90
4	88
5	85

(2CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1650 (C=O, s), 1586 (C=C, m), 769 (CH, m); MS (70 Ev, EI) m/z = 270 (M⁺), 135, 120, 107, 104, 76.

Compound (c) 4-Dimethylaminobenzil: UV (CH₃OH) λ_{\max} : 229 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 3.38 (s, 6H, CH₃), 6.67 (d, 2H, CH, J = 5.2 Hz), 7.48 (d, 2H, CH, J = 8.1 Hz), 7.61 (d, 2H, CH, J = 8.1 Hz), 7.8 (d, H, CH, J = 8.1 Hz), 8.28 (d, 2H, CH, J = 5.2 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 55.91 (2CH₃), 111.20 (2CH), 128.90 (2CH), 129.01 (C), 129.70 (2CH), 135.37 (CH), 135.50 (C), 141.47 (C), 153.76 (C), 196.72 (CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1650, 1700 (C=O, s), 1440, 1620 (C=C, m), 705 (CH, m); MS (70 Ev, EI) 252 (M⁺), 148, 120, 104, 76.

Compound (d), 4,4'-dimethylbenzil: UV (CH₃OH) λ_{\max} : 225 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 2.45 (s, 6H, CH₃), 7.4 (d, 4H, CH, J = 7.2 Hz), 7.75 (d, 4H, CH, J = 7.6 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 21.95 (2CH₃), 129.72 (4CH), 130.03 (4CH), 130.69 (2C), 146.11 (2C), 194.54 (2CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1650, (C=O, s), 1586 (C=C, m), 769 (CH, m); MS (70 Ev, EI) 238 (M⁺), 119, 104, 91, 76.

Compound (e), 4-Methoxybenzil: UV (CH₃OH) λ_{\max} : 228 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 3.76 (s, 3H, OCH₃), 6.82 (2H, d), 7.34–7.61 (5H, m), 7.86 (2H, d) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 55.19 (CH₃), 113.20 (2CH), 128.90 (2CH), 129.70 (2CH), 130.30 (C), 131.37 (CH), 133 (2CH), 133.26 (C), 164.69 (C), 194.30 (CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1650, (C=O, s), 1586 (C=C, m), 769 (CH, m); MS (70 Ev, EI) 239 (M⁺), 135, 107, 104, 76.

Compound (f), 2-pyridil: UV (CH₃OH) λ_{\max} : 365 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 7.49 (t, 2H, CH, J = 8.1 Hz), 7.91

(t, 2H, CH, J = 8.1 Hz), 8.18 (d, 2H, CH, J = 8.1 Hz), 8.56 (d, 2H, CH, J = 8.1 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 122.27 (2CH), 127.99 (2CH), 137.26 (2CH), 149.46 (2CH), 151.65 (2C), 197.02 (2CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1713 (C=O, s), 1274 (C=N, s), 1505 (C=C, m); MS (70 Ev, EI) m/z = 212 (M⁺), 106, 78.

Compound (g), 2,2',4,4'-tetramethoxybenzil: UV (CH₃OH) λ_{\max} : 226 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 3.88 (s, 3H, OCH₃), 3.90 (s, 3H, OCH₃), 6.44 (s, 2H, CH), 6.53 (d, 2H, CH, J = 8.4 Hz), 7.81 (d, 2H, CH, J = 8.8 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 55.23 (OCH₃), 55.80 (OCH₃), 101.58 (2CH), 113.03 (2CH), 116.91 (2C), 131.22 (2CH), 161.83 (2C), 162.93 (2C), 186.91 (2CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1630–1680 (C=O, s), 1470, 1618 (C=C, m), 738 (CH, m); MS (70 Ev, EI) m/z = 330 (M⁺), 167, 135, 107, 104, 76.

Compound (h), 3-Methoxybenzil: UV (CH₃OH) λ_{\max} : 234 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 3.72 (s, 3H, OCH₃), 7.01 (1H, t), 7.1 (1H, s), 7.32 (1H, d), 7.51 (2H, t), 7.60 (1H, t), 7.72 (2H, d) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 54.00 (OCH₃), 116.80 (CH), 120.13 (CH), 124.16 (CH), 128.90 (2CH), 129.70 (2CH), 131.05 (CH), 131.37 (CH), 132.88 (C), 135.27 (C), 163.09 (C), 193.41 (CO), 194.30 (CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1660, (C=O, s), 1396, 1613 (C=C, m), 725 (CH, m); MS (70 Ev, EI) 239 (M⁺), 135, 107, 104, 76.

Compound (i), 4-Methylbenzil: UV (CH₃OH) λ_{\max} : 223 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 2.34 (s, 3H, CH₃), 7.3 (m, 2H), 7.35 (m, 2H), 7.42 (t, 1H, J = 8 Hz), 7.55 (t, 2H, J = 8, 7.2 Hz), 7.92 (d,d, 2H, J = 7.92, 1.2 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 22.06 (CH₃), 122.71 (2CH), 130.12 (2CH), 130.28 (2CH), 131.18 (2CH), 132.54 (2CH), 133.17 (C), 133.83 (C), 147.02 (C), 193.95 (CO), 194.08 (CO) ppm; IR (KBr, ν_{\max} , cm⁻¹): 1640, 1680, (C=O, s), 1420, 1630 (C=C, m), 724 (CH, m); MS (70 Ev, EI) 223 (M⁺), 119, 104, 76.

Compound (j), 3-Bromo-4'-methylbenzil: UV (CH₃OH) λ_{\max} : 227 nm; ¹H NMR (CDCl₃, 400 MHz) δ : 2.42 (s, 3H, CH₃), 7.34 (t, 1H, CH), 7.61 (d, 1H, CH), 7.74 (d, 3H, 3CH), 8.04 (s, H, CH), 8.59 (s, 1H, CH), 8.65 (s, 1H, CH) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 55.65 (CH₃), 144.44 (2CH), 123.21 (C), 129.12 (CH), 129.76 (C), 130.47 (2CH), 131.37 (CH), 132.44 (CH), 134.91 (CH), 137.46 (C), 165.18 (C),

192.04 (CO), 193.08 (CO) ppm; IR (KBr, ν_{\max} , cm^{-1}): 1640, 1700, (C=O, s), 1420, 1620 (C=C, m), 705, 730 (CH, m); MS (70 Ev, EI) 319 (M^+), 193, 119, 104, 76.

5. Conclusions

In summary, we have found a facile and efficient method for the oxidation of symmetrical and unsymmetrical benzoin to corresponding benzils using with the environmentally friendly H_2O_2 as a sole oxidant and of Mn(II) Schiff base complex as catalyst under milder conditions. The Schiff base complex exhibited good catalytic activity in the oxidation of various benzil derivatives with hydrogen peroxide. The present procedure has many advantages such as short reaction times, mild conditions, easy operation procedures, easy removal catalyst, and high yields.

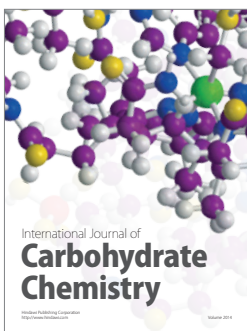
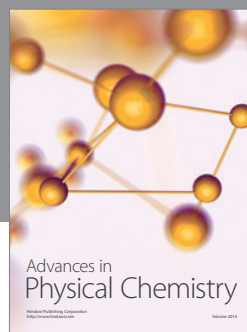
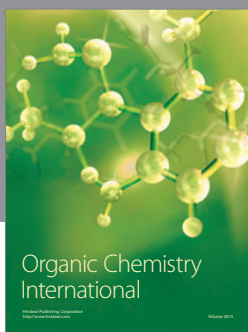
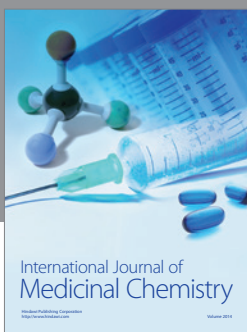
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