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Highly efficient and selective oxidation of secondary alcohols to ketones under organic solvent and transition metal free conditions

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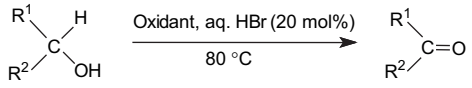
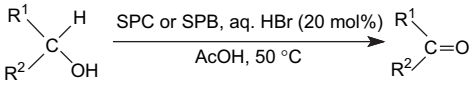
Abstract—The aqueous HBr/H_2O_2 was found to be highly efficient and green catalytic system for the selective oxidation of the secondary alcohols to ketones in excellent yields under organic solvent free conditions. The results of the oxidation of the secondary alcohols with solid alternatives of the aqueous hydrogen peroxide like SPC or SPB are also described.

1. Introduction

The development of catalytic synthetic methodologies using clean oxidants like molecular oxygen and hydrogen peroxide with a view to replace environmentally prohibitive stoichiometric oxidants is an area of current interest.[1] Hydrogen peroxide is an attractive, atom-economic, and environmentally benign oxidant as it is cheap, easily available, and produces only water as by-product. In the recent years, it has been extensively used in developing a variety of synthetically important oxidation methodologies like epoxidation, oxidation of alcohols, aldehydes, and sulfides using transition metal based catalysts both in homogeneous and heterogeneous phases.[2] The oxidation of secondary alcohols to carbonyl compounds is an important synthetic transformation[1a,3] and a variety of transition metal based catalysts, such as methyltrioxorhenium[4] dinuclear iron complexes,[5] vanadium phosphorus oxide,[6] cobalt(II) complexes,[7] Fe^{3+}/montmorillonite-K10 system,[8] and sodium tungstate[9] using hydrogen peroxide as oxidant, have been reported in the literature to accomplish it. However, most of these methods are associated with the limitations such as use of toxic, expensive metals, lower yields of the products, and oxidation of only activated such as benzylic and allylic alcohols. In the recent past, increasing emphasis is being placed toward the development of transition metal free ecofriendly synthetic methodologies to avoid the use of toxic and expensive metals and their complexes. In our preliminary communication,[10] we have reported a new and highly efficient methodology for the oxidation of secondary alcohols to ketones with aqueous H_2O_2 in the presence of catalytic amounts of HBr under very mild conditions. Our further observation that this system works more efficiently under organic solvent free conditions prompted us to describe the full details of this improved protocol along with the applications of solid oxidants in the place of aqueous hydrogen peroxide (Schemes 1 and 2).



Scheme 1.



Scheme 2.

2. Results and discussion

The oxidation of various secondary alcohols, both activated and non-activated, was carried out by heating the reaction mixture of substrate (1 mmol), aqueous 30 wt % hydrogen peroxide (2 mmol), and catalytic amount of aqueous HBr (20 mol %) at 80 °C under organic solvent free conditions. All the alcohols were selectively converted to the corresponding ketones in excellent yields and these results are presented in Table 1. Among the various alcohols studied, benzoins were found to be the most reactive and required shorter reaction times for their oxidation (Table 1, entries 17 and 18). Furthermore, aromatic substituted alcohols were found to be more reactive than aliphatic/alicyclic (Table 1, entries 1 and 2). Alcohols having both secondary

Keywords: Oxidation; Secondary alcohols; Ketones; Solid oxidant.
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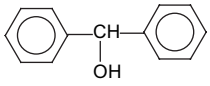
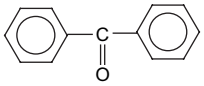
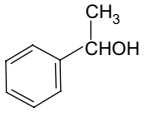
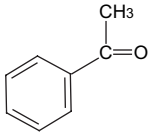
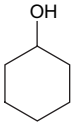
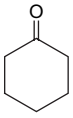
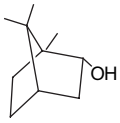
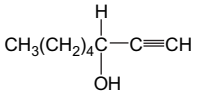
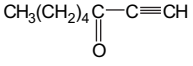
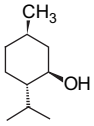
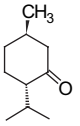
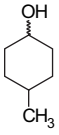
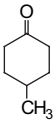
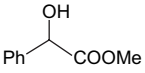
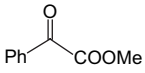
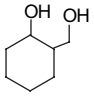
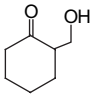
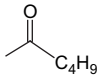
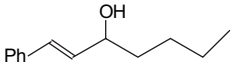
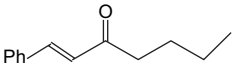
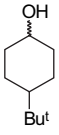
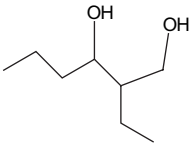
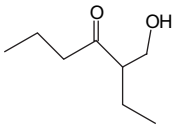
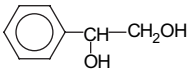
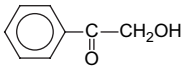
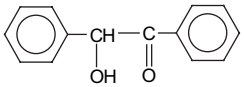
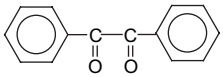
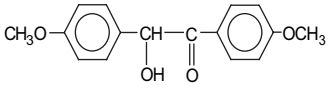
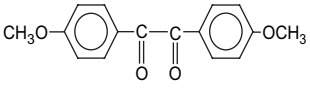
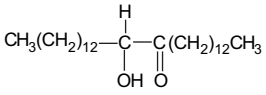
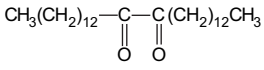
Table 1. Oxidation of secondary alcohols to ketones

Entry	Substrate	Product	Method A		Method B	
			Reaction time (h)	Yield[a]	Reaction time (h)	Yield[a]
1			0.50	98	1.0	96
2			0.75	94	1.0	90
3			2.0	89	2.0	80
4			3.5	75	3.0	72
5			5.00	82	5.5	75
6			4.50	76	4.0	70
7			2.5	85	3.5	82
8			1.75	82	2.0	80
9			2.0	89	2.5	86
10			2.0	87	2.75	84
11			1.5	82	2.5	80
12			3.5	75	4.0	70
13			2.75	85	3.5	82

(*continued*)

Table 1. (*continued*)

Entry	Substrate	Product	Method A		Method B	
			Reaction time (h)	Yield[a]	Reaction time (h)	Yield[a]
14			3.50	88	5.5	84
15			4.5	78	5.5	74
16			1.75	88	2.50	85
17			0.15	98	0.25	96
18			0.25	97	0.33	96
19			2.5	89	3.5	80

Method A—Reaction conditions: secondary alcohol (1 mmol), 30% H_2O_2 (2 mmol), and 48% aqueous HBr (20 mol %) at 80 °C under organic solvent free conditions.
Method B—Reaction conditions: secondary alcohol (1 mmol), 70% TBHP (2.5 mmol), and 48% aqueous HBr (20 mol %) at 80 °C under organic solvent free conditions.
[a] Isolated yields.

as well as primary hydroxyl groups such as 2-ethyl-1,3-hexanediol, 2-hydroxymethylcyclohexanol, and 1-phenyl-1,2-ethanediol were selectively converted into 2-ethyl-1-hydroxy-3-hexanone, 2-hydroxymethylcyclohexanone, and 2-hydroxy-1-phenylethanone, respectively, under these conditions, showing the usefulness of this method for the selective oxidation of secondary alcohols in the presence of primary alcohols (Table 1, entries 10, 15, and 16). Similarly, other functional groups such as double and triple bonds were found to be inert under these conditions (Table 1, entries 5 and 12). To evaluate the efficiency of this method, we also carried out the oxidation of benzhydrol to benzophenone in different organic solvents and these results are shown in Table 2. Although among the various organic solvents studied, acetonitrile was found to be more suitable, but in general, organic solvent free condition was found to be the best and required shorter reaction time. The effect of the reaction temperature was also evaluated and found that the oxidation of benzhydrol to benzophenone was slow at room temperature but could be conducted efficiently at 80 °C. Further increase in temperature affected the oxidation adversely in terms of yield of the benzophenone, probably due to fast decomposition of H_2O_2 at higher temperature.

Table 2. Effect of various solvents[a]

Entry	Substrate	Solvent	Method A		Method B	
			Reaction time (h)	Yield[b]	Reaction time (h)	Yield[b]
1	Benzhydrol	Acetonitrile	0.75	92	1.5	94
2	Benzhydrol	Methanol	2.0	40	3.0	35
3	Benzhydrol	Toluene	4.5	35	5.0	42
4	Benzhydrol	Dichloroethane	1.5	85	2.5	80
5	Benzhydrol	Neat	0.50	98[c]	1.0	96[c]

[a] Reaction conditions: substrate (1 mmol), 30% H_2O_2 (2 mmol), and 48% aqueous HBr (20 mol %), solvent (3 ml) under refluxing condition.
[b] Isolated yield.
[c] As mentioned in Table 1.

2.1. Effect of various bromine sources

To evaluate the effect of various bromine sources, the oxidation of benzhydrol was studied using catalytic amount of different bromine sources (20 mol %) in place of aqueous HBr with aqueous 30% hydrogen peroxide as an oxidant under similar reaction conditions and the results are presented in Table 3. Although the use of molecular bromine and

Table 3. Effect of various bromine sources under neat conditions[a]

Entry	Substrate	Bromine source	Reaction times (h)	Yields (%)[b]
1	Benzhydrol	Aqueous HBr	0.5	98
2	Benzhydrol	Br_2	0.5	94
3	Benzhydrol	NaBr	4.0	30
4	Benzhydrol	KBr	4.0	85
5	Benzhydrol	$KBr+V_2O_5$	1.5	85[c]
6	Benzhydrol	$PyHBr_3$	1.0	92

[a] Reaction conditions as mentioned in Table 1.
[b] Isolated yields.
[c] Using acetonitrile as solvent.

pyridiniumhydrobromide perbromide yielded comparable results, the use of salts such as NaBr and KBr gave very poor yield of the benzophenone. It was also observed that the addition of the catalytic amount of vanadium pentoxide in the reaction mixture of benzhydrol and aqueous H_2O_2 containing catalytic amount of KBr, accelerated the reaction rate and the oxidation was completed within 1.5 h (Table 3, entry 5).

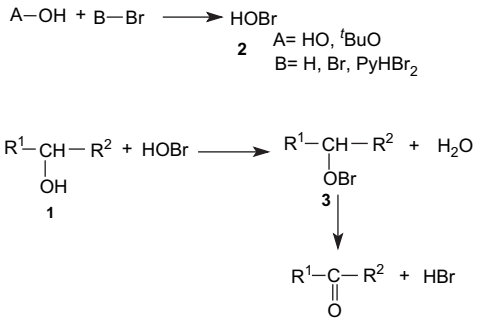
2.2. Effect of various oxidants

Further with a view to evaluate the efficiency of other oxidants, the oxidation of benzhydrol was carried out with molecular oxygen and aqueous 70% *tert*-butylhydroperoxide in the presence of catalytic amount of aqueous HBr under similar reaction conditions. While the reaction did not proceed with molecular oxygen, the use of TBHP as an oxidant yielded results comparable to aqueous H_2O_2. To evaluate the relative efficiencies of TBHP and aqueous H_2O_2 as oxidants, we studied the oxidation of various activated and non-activated alcohols with 70% TBHP in the presence of catalytic amount of aqueous HBr under organic solvent free conditions and the results obtained are presented in Table 1. All the alcohols were selectively converted to the corresponding ketones and reactivity order was found to be the same as obtained by using H_2O_2 as an oxidant. Benzoins in general were again found to be the most reactive while alcohols containing aromatic substituents were found to be more reactive than aliphatic/alicyclic alcohols. Oxidation of benzhydrol when carried out with TBHP in different solvents yielded results similar to hydrogen peroxide and again organic solvent free condition was found to be the most efficient. (Table 2).

The use of solid peroxy compounds, such as sodium perborate (SPB) and sodium percarbonate (SPC) due to their storage stability, crystalline nature, ease of handling, and higher hydrogen peroxide contents, has gained considerable attention in the recent years in various chemical transformations.[11] We therefore studied the oxidation of secondary alcohols to ketones with these solid oxidants using catalytic amount of aqueous HBr (Scheme 2). The protocol developed consists of oxidation of secondary alcohol (1 mmol) with solid oxidant (SPC/SPB) (2.5 mmol) in the presence of catalytic amount of aqueous HBr (20 mol %) in acetic acid (10 mmol) at 50 °C without using any organic solvent as reaction media (Table 4). All the alcohols were selectively and efficiently converted to the corresponding ketones in excellent yields. The presence of acetic acid was found to be essential in these reactions and in its absence the oxidation of benzhydrol in acetonitrile under similar reaction conditions was found to be very slow and gave poor yield of the benzophenone (Table 4, entry 1). This is probably due to the fast release of hydrogen peroxide from the solid oxidants in the presence of acetic acid.[12] To examine the effect of temperature, oxidation of benzhydrol was carried out at different reaction temperatures under similar reaction conditions, using SPC and SPB as solid oxidants. While the reaction was found to be slow at room temperature, at 50 °C the reaction rate was maximum and further increase in the reaction temperature decreases the reaction rate and afforded poor yield of the benzophenone probably due to faster decomposition of solid oxidants at higher temperature.[13]

It is worth mentioning that in contrast to aqueous H_2O_2 and SPC, sodium perborate could oxidize benzhydrol to benzophenone in the presence of catalytic amount of KBr (20 mol %) using acetic acid as a solvent (Table 4, entry 3).

The plausible mechanistic pathway for these reactions may involve the formation of hypobromous acid **2** by the reaction of peroxide oxidant with hydrobromic acid,[10] and its reaction with secondary alcohol **1** to afford hypobromite species **3** which on abstraction of hydrogen yielded corresponding ketone as shown in Scheme 3.



Scheme 3.

3. Conclusion

In summary, the present method describes an efficient, selective, and environmentally friendly synthetic methodology for the oxidation of various secondary alcohols to ketones under transition metal and organic solvent free conditions. The use of SPC and SPB as solid oxidants due to their ease of synthesis/handling, storage stability, and high hydrogen peroxide content makes it more advantageous than previously reported methods. Furthermore, the simplicity of the system, versatility toward a range of activated and non-activated alcohols, selective oxidation of secondary alcohols in the presence of primary alcoholic and other functional groups, simple reaction conditions, and excellent yields of the products make this method a facile, ideal, and attractive synthetic tool for the oxidation of secondary alcohols to ketones.

4. Experimental

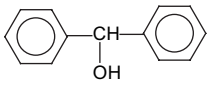
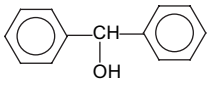
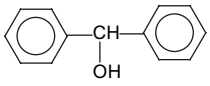
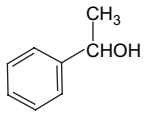
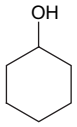
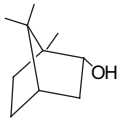
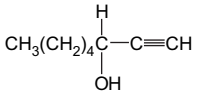
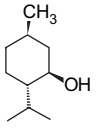
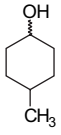
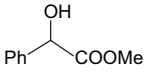
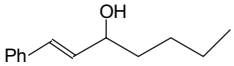
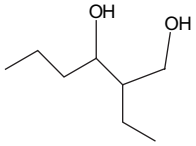
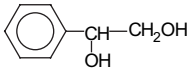
4.1. General

The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on Bruker 300 MHz spectrometer and the chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane (TMS) as an internal standard. The IR spectra were recorded on a Perkin–Elmer FTIR X 1760 instrument.

4.2. General experimental procedure for the oxidation of secondary alcohols using aqueous HBr/H_2O_2 system

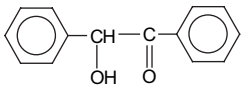
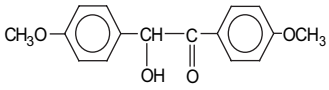
To a stirred solution of secondary alcohol (1 mmol) and aqueous 30% H_2O_2 (2 mmol) was added aqueous HBr (20 mol %) and the mixture was heated at 80 °C under organic solvent free conditions for the period given in

Table 4. Oxidation of secondary alcohols with solid oxidants SPC and SPB

Entry	Substrate	Method A		Method B	
		Reaction time (h)	Yield[a]	Reaction time (h)	Yield[a]
1		4.5	45	6.5	40[b]
2		1.0	96	1.5	94
3		—	—	1.25	90[c]
4		1.5	92	1.5	90
5		3.00	90	3.75	86
6		5.0	82	6.5	80
7		6.5	82	4.5	75
8		5.70	72	6.0	70
9		5.70	72	6.0	70
10		3.5	85	4.5	80
11		2.5	82	2.5	78
12		5.0	75	6.5	69
13		5.5	72	6.0	74

(*continued*)

Table 4. (*continued*)

Entry	Substrate	Method A		Method B	
		Reaction time (h)	Yield[a]	Reaction time (h)	Yield[a]
14		2.0	89	3.50	82
15		0.25	97	0.25	94

Method A—Reaction conditions: secondary alcohol (1 mmol), 48% aqueous HBr (20 mol %), SPC (2.5 mmol), and acetic acid (10 mmol) at 50 °C under organic solvent free conditions.
Method B—Experiments carried out with SPB.
[a] Isolated yields.
[b] Experiment carried out in acetonitrile without acetic acid.
[c] Experiment was carried out using KBr instead of aqueous HBr without any catalyst.

Table 1. Progress of the reaction was monitored by TLC (SiO_2). At the end of the reaction the excess hydrogen peroxide was destroyed by aqueous bisulfite followed by filtration through a Buckner funnel. After filtration, the reaction mixture was taken in dichloromethane and organic layer was washed with water (three times). The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under vacuum to afford crude product, which was purified by column chromatography on silica gel using ethyl acetate/hexane (9:1) as an eluent. Evaporation of the solvent yielded corresponding ketones. Reaction times and yields of the products are given in Table 2.

4.3. Typical experimental procedure for oxidation of secondary alcohols using aqueous HBr/solid oxidant system

In a stirred mixture of benzhydrol (0.18 g, 1 mmol), SPB (0.39 g, 2.5 mmol), and acetic acid (0.6 ml, 10 mmol) was added dropwise aqueous HBr (20 mol %, 0.2 mmol, 0.03 ml) at 50 °C. The mixture was stirred for 2 h. After completion of the reaction, the solvent was evaporated under vacuum. The residue thus obtained was extracted with water and dichloromethane. The organic layer was removed and washed again with water (two times). Finally, the organic layer was removed and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to yield pure benzophenone (0.171 g, 94%). All the products were identified by comparing their physical and spectral data (IR and ^{1}H NMR) with the literature values. The physical and spectral data of the products are given below.

Benzophenone (Table 1, entry 1):[14] mp 47 °C (lit. 48–49 °C)[15] IR (KBr): 3028, 1661, 1489, 1204, 1151 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 7.30–7.55 (m, 6H, Ar H), 7.90–8.00 (m, 4H, Ar H).

Acetophenone (Table 2, entry 2):[16] oil, IR (KBr): 3086, 2923, 1685, 1430, 1267, 1160 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 2.50 (s, 3H, CH_3), 7.45–7.85 (m, 5H, Ar H).

Cyclohexanone (Table 1, entry 3):[14] bp 153 °C/760 mm (lit. 155 °C/760 mm)[15] IR (KBr): 2940, 1712, 1449, 1235 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 1.80–2.15 (m, 6H, CH_2), 2.30–2.38 (m, 4H, CH_2).

(±)-Camphor (Table 1, entry 4):[17] mp 172–173 °C (lit. 175–177 °C)[15] IR (KBr): 2935, 1715, 1440, 1369 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 0.97 (s, 6H, CH_3), 1.05–1.40 (m, 5H, CH_2, CH), 1.90 (s, 3H, CH_3), 2.10–2.20 (m, 2H, CH_2).

1-Octyne-3-one (Table 1, entry 5): oil, IR (KBr): 3278, 2950, 2105, 1680, 1180 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 0.89–0.95 (m, 3H CH_3), 1.10–1.40 (m, 6H, CH_2), 2.30–2.35 (m, 2H, CH_2), 3.10 (s, 1H, ≡CH).

(−)-Menthone (Table 1, entry 6):[14] bp 203–204 °C/760 mm (lit. 207–210 °C/760 mm)[15] IR (KBr) 2940, 1710, 1443, 1369 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 0.80–0.95 (m, 10H, CH_3, CH_2), 1.38–1.75 (m, 5H, CH_2, CH), 2.18–2.52 (m, 3H, CH_3).

4-Methylcyclohexanone (Table 1, entry 7):[18] colorless oil, IR (KBr): 2932, 2869, 1720, 1156 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 0.92 (d, J=6.8 Hz, 3H, CH_3), 1.10–1.25 (m, 5H, CH_2, CH), 1.24–1.32 (m, 4H, CH_2).

Methyl benzoylformate (Table 1, entry 8):[19] bp 247–248 °C (lit. 248–250 °C/760 mm),[15] IR (KBr): 3076, 2941, 1740, 1680, 1315, 1204. ^{1}H NMR ($CDCl_3$) δ ppm: 3.95 (s, 3H, CH_3), 7.40–8.20 (m, 5H, Ar H).

2-Methylcyclohexanone (Table 1, entry 9):[18] colorless oil, IR (KBr): 2935, 2863, 1718, 1370, 1156 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 1.00 (d, J=7.0 Hz, 3H, CH_3), 1.34–1.36 (m, 6H, CH_2), 1.62–1.80 (m, 3H).

2-Hydroxymethylcyclohexanone (Table 1, entry 10):[20] colorless oil, IR (KBr) 3421, 2960, 1710, 1169 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 1.36–2.61 (m, 9H, CH_2), 2.79 (br s, 1H, OH), 3.50–3.67 (m, 2H, CH_2).

Hexan-2-one (Table 1, entry 11):[16] oil, IR (KBr): 2961, 2937, 1718, 1368, 1165 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 0.90 (t, J=7.2 Hz, 3H, CH_3), 1.27–1.32 (m, 2H, CH_2), 1.52–1.58 (m, 2H), 2.14 (s, 3H, CH_3) 2.43 (t, J=7.2 Hz, 2H, CH_2).

1-Phenyl-1-hepten-3-one (Table 1, entry 12):[21] colorless oil, IR (KBr): 3010, 2961, 2937, 1720, 1364, 1162 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ ppm: 0.90 (t, J=7.0 Hz, 3H, CH_3), 1.35–1.55 (m, 4H, CH_2), 2.58 (t, J=6.2 Hz, 2H, CH_2),

6.74 (d, 1H, J=13.2 Hz, =CH), 7.28–7.60 (m, 6H, =CH and Ar H).

4-tert-Butyl cyclohexanone (Table 1, entry 13):[23a,24a] mp 45–47 °C (lit. 47–50 °C)[15] IR (KBr): 2955, 1718, 1468, 1366 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 0.90 (s, 9H, CH_3), 1.30–1.60 (m, 5H), 2.10–2.35 (m, 4H).

Cyclopentanone (Table 1, entry 14):[23b,24b] bp 129–130 °C/760 mm (130–131 °C/760 mm)[15] IR (KBr) 2942, 1446, 1236 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.82–210 (m, 4H, CH_2), 2.34–2.40 (m, 4H, CH_2).

3-Hydroxymethyl-4-heptanone (Table 1, entry 15):[20] colorless liquid. IR (KBr): 3422, 1705 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 0.90 (t, J=7.4 Hz, 3H, CH_3), 0.95 (t, J=7.5 Hz, 3H, CH_3), 1.39–1.70 (m, 4H, CH_2), 2.14 (br s, 1H, OH), 2.45 (t, J=7.3 Hz, 2H, CH_2), 2.60–2.68 (m, 1H, CH), 3.70–3.75 (m, 2H, CH_2).

2-Hydroxy-1-phenylethanone (Table 1, entry 16):[22] mp 83–84 °C (lit. 84–85 °C) IR (KBr): 3428, 1682 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 2.98 (s, 1H, OH), 4.85 (s, 2H, CH_2), 7.50–7.85 (m, 5H, Ar H).

Benzil (Table 1, entry 17):[14] mp 92–93 °C (lit. 94–95 °C)[15] IR (KBr): 3043, 1678, 1659, 1594, 1315, 1176 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 7.52–7.61 (m, 6H, Ar H), 7.80–7.89 (m, 4H, Ar H).

4,4′-Dimethoxybenzil (Table 1, entry 18):[25] mp 130–131 °C (lit. 132–134 °C)[15] IR (KBr): 3046, 2959, 1682, 1598, 1314, 1171 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 3.80 (s, 6H, CH_3), 6.94 (d, J=8.0 Hz, 4H, Ar H), 7.94 (d, J=8.0 Hz, 4H, Ar H).

14,15-Octacosanedione (Table 1, entry 19): mp 67–69 °C (lit. 70–72 °C)[26] IR (KBr) 2941, 2877, 1724, 1449, 1389, 1163 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 0.89–1.00 (m, 6H, CH_3), 1.10–1.72 (m, 44H, CH_2), 2.30 (m, 4H, CH_2).

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