Iodobenzene Dichloride as a Stoichiometric Oxidant for the Conversion of Alcohols into Carbonyl Compounds; Two Facile Methods for Its Preparation

Xue-Fei Zhao, Chi Zhang*

The State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. of China
Fax +86(22)23499247; E-mail: zhangchi@nankai.edu.cn

Received 15 September 2006; revised 8 November 2006

Abstract: A highly efficient and mild procedure is described for the oxidation of different types of alcohols using 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) as the catalyst, iodobenzene dichloride ($PhICl_2$) as a stoichiometric oxidant, and pyridine as the base. This procedure also smoothly oxidizes 1,2-diols to α-hydroxy ketones or α-diketones depending upon the amount of iodobenzene dichloride used. A competitive study shows that using the 2,2,6,6-tetramethylpiperidin-1-yloxy/iodobenzene dichloride/pyridine system aliphatic secondary alcohols are preferentially oxidized over aliphatic primary alcohols. In addition, two very convenient and high yielding procedures for the preparation of iodoarene dichlorides from iodoarenes have been developed. One employs solid sodium chlorite as a chlorinating agent in dilute hydrochloric acid solution; the other uses sodium hypochlorite as a chlorinating agent still in hydrochloric acid solution, which is more robust than the sodium chlorite system. Typically, the preparation of iodobenzene dichloride from iodobenzene was performed in five minutes using the sodium hypochlorite/hydrochloric acid system.

Key words: iodobenzene dichloride, alcohols, catalysis, TEMPO, oxidation

Iodobenzene dichloride, the first reported hypervalent iodine reagent, was synthesized by C. Willgerodt in 1886.[1] Historically, it has been principally used as a chlorinating reagent in organic synthesis replacing gaseous chlorine.[2] Typically, Garvey, Halley, and Allen first observed that the reaction of iodobenzene dichloride with unsaturated hydrocarbons in refluxing 1,2-dichloroethane gave the same products as when chlorine gas was used.[3] Breslow et al. have shown a number of beautiful examples of template-directed chlorination of the C–H bond in steroids using iodobenzene dichloride as the chlorinating agent.[4] Moreover, numerous applications of iodobenzene dichloride for the introduction of element chlorine into various metal complexes have also been described.[5] Another impressive use of iodobenzene dichloride is its combination with lead(II) thiocyanate to effect the thiocyanation of various organic substrates including silyl enol ethers,[6] β-dicarbonyl compounds,[6] alkynes,[7] phenols and naphthols.[8] However, it appeared that the synthetic utility of iodobenzene dichloride as an oxidizing agent was fairly limited; the oxidation of aldoximes to nitrile oxides[9] and oxidative deoximation of ketoximes to the corresponding ketones[10] are two examples. In addition, Wicha et al. reported that iodobenzene dichloride oxidized secondary alcohols to the corresponding ketones in moderate yields in the presence of pyridine.[11] The main drawback to this simple system was its inability to oxidize primary alcohols to the corresponding aldehydes. Herein, we report the use of a 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) catalyzed oxidation system with iodobenzene dichloride as the stoichiometric oxidant and pyridine as the base for the oxidization of primary and secondary alcohols to the corresponding aldehydes and ketones in excellent yields. We also report two efficient, easily handled, and environmentally benign procedures for the preparation of iodoarene dichlorides from iodoarenes.

In the course of investigating the oxidative properties of iodobenzene dichloride, we found that decan-1-ol was oxidized to decanal in quantitative yield with TEMPO (8 mol%), iodobenzene dichloride (1.5 equiv), and pyridine (3 equiv) in chloroform (10 mL) at 50 °C (oil bath) for six hours. Reducing the loading of catalyst TEMPO from 8 mol% to 5 mol% resulted in a decreased yield of decanal (82%). When the reaction was carried out at room temperature, the yield of decanal was 80% even after 18 hours. The concentration effect was apparent in this reaction since the reaction time was shortened from six to three hours when the volume of chloroform was reduced from 10 mL to 5 mL. In addition, in the absence of pyridine, the conversion of decan-1-ol was only 54% and decanal was obtained in 48% yield after 18 hours. The solvent effect on the oxidation of decan-1-ol was also examined, the results are summarized in Table 1.

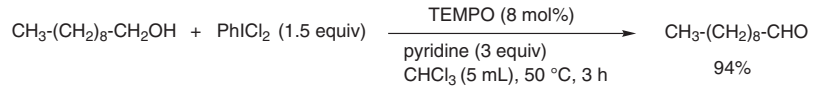
As shown in Table 1, chloroform appears to be the best solvent among those tested, affording decanal in 94%

Table 1 Screened Solvents for the Oxidation of Decan-1-ol[a]

Entry	Solvent	Time (h)	Yield (%)
1	$CHCl_3$	3	94
2	CH_2Cl_2	3	50
3	THF	3	69
4	PhMe	3	62
5	EtOAc	3	56
6	MeCN	3	57

[a] Reactions were performed with decan-1-ol (1 mmol), TEMPO (8 mol%), $PhICl_2$ (1.5 equiv), pyridine (3 equiv), solvent (5 mL), 50 °C.

SYNTHESIS 2007, No. 4, pp 0551–0557
Advanced online publication: 12.01.2007
DOI: 10.1055/s-2007-965889; Art ID: F15306SS



Scheme 1 Optimal reaction conditions for the oxidation of decan-1-ol

yield (Table 1, entry 1). The yield of decanal was only 50% when reaction was performed in dichloromethane; a major factor in this case was the poor solubility of iodobenzene dichloride in dichloromethane (Table 1, entry 2). Consequently, the optimal reaction parameters were fixed and are given in Scheme 1.

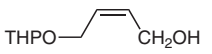
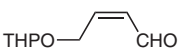
A variety of alcohols, such as aliphatic primary and secondary alcohols, benzylic and allylic alcohols, were oxidized to the corresponding carbonyl compounds in good to excellent yields. Like decan-1-ol, two other aliphatic primary alcohols with shorter or longer carbon chains, octan-1-ol and hexadecan-1-ol were smoothly oxidized to their corresponding aldehydes in excellent yields (Table 2, entries 2 and 3). As for secondary alcohols, octan-2-ol and menthol were oxidized to the corresponding ketones in 98% and 93% yields, respectively (Table 2, entries 4 and 5). 1-Phenylethanol and benzyl alcohol were excellent substrates under the standard oxidation conditions since their corresponding products were obtained in 94% and quantitative yield, respectively (Table 2, entries 6 and 7). Notably, (2*Z*)-4-(tetrahydropyran-2-yloxy)but-2-en-1-ol was oxidized to the corresponding aldehyde in 77% yield without isomerization of the double bond (Table 2, entry 8).

The iodobenzene diacetate/TEMPO system developed by Piancatelli et al. performs very well for the oxidization of various primary and secondary alcohols and 1,3-diols to their corresponding carbonyl compounds; 1,2-diols are, however, cleaved to give the corresponding aldehydes.[12] In our system, 1,2-diols could be successfully oxidized to their corresponding α-hydroxy ketones or α-diketones depending upon the number of equivalents of iodobenzene dichloride used. For example, cyclooctane-1,2-diol was oxidized using 1.1 equivalents of iodobenzene dichloride to give 2-hydroxycyclooctan-1-one in 85% yield together with cyclooctane-1,2-dione in 10% yield (Table 3, entry 1). Increasing the amount of iodobenzene dichloride to three equivalents gave cyclooctane-1,2-dione in quantitatively yield as the sole product (Table 3, entry 2). In the case of 1,2-diphenylethane-1,2-diol, as benzil is more stable than benzoin due to the conjugate effect, the ratio of α-hydroxy ketone (benzoin) to α-diketone (benzil) is only 1.9:1 with 1.1 equivalents of iodobenzene dichloride, which is much lower than in the case of cyclooctane-1,2-diol (1.9:1 vs 8.5:1; Table 3, entry 3 vs entry 1).

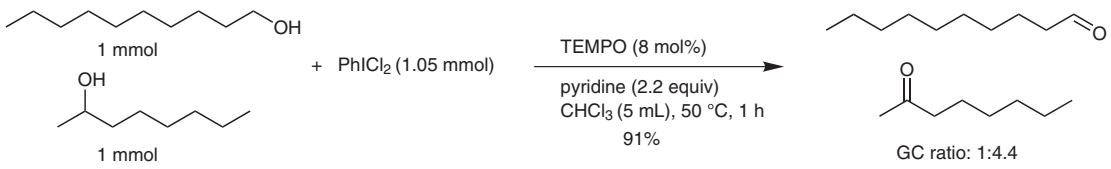
It was observed that longer reaction times were required for the oxidation of primary aliphatic alcohols compared with that for a secondary alcohol (Table 2, entries 1, 2, and 3 vs entry 4). A competitive study was conducted in which a mixture of decan-1-ol (1 mmol) and octan-2-ol (1 mmol) was oxidized using 1.05 mmol of iodobenzene dichloride and decanal and octan-2-one were obtained in a 1:4.4 ratio. This finding confirmed that the TEMPO/iodobenzene dichloride/pyridine oxidation system preferentially oxidizes secondary alcohols over primary alcohols (Scheme 2). It should be noted that iodobenzene diacetate/TEMPO preferentially oxidizes primary alcohols over secondary alcohols.[12]

The mechanism of this alcohol oxidation reaction is worth discussing. Firstly, the fact that the efficiency of this reaction decreased dramatically in the absence of pyridine suggested that this reaction is not an acid-catalyzed TEMPO dismutation process to give an oxoammonium salt, which operated in a fairly similar oxidation system, iodobenzene diacetate/TEMPO.[12] Accordingly, it is proposed that TEMPO is oxidized to its oxoammonium salt, which, as previously reported, is capable of oxidizing al-

Table 2 Oxidation of Various Alcohols with Iodobenzene Dichloride[a]

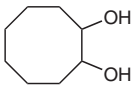
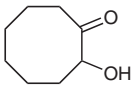
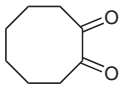
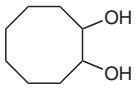
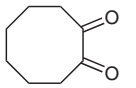
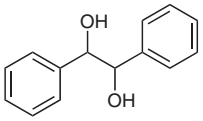
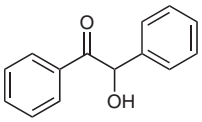
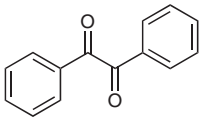
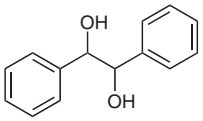
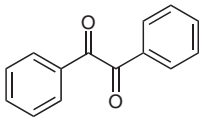
Entry	Alcohol	Time	Product	Yield[b] (%)
1	decan-1-ol	3 h	decanal	94
2	octan-1-ol	3 h	octanal	89
3	hexadecan-1-ol	4.5 h	hexadecanal	92
4	octan-2-ol	1 h	octan-2-one	98
5	menthol	45 min	menthone	93
6	1-phenylethanol	40 min	acetophenone	94
7	benzyl alcohol	40 min	benzaldehyde	>99[c]
8		1.5 h		77

[a] Reaction conditions: alcohol (1 mmol), TEMPO (8 mol%), $PhICl_2$ (1.5 equiv), pyridine (3 equiv), $CHCl_3$ (5 mL), 50 °C
[b] Isolated yield.
[c] GC yield.



Scheme 2 Competitive reaction between decan-1-ol and octan-2-ol

Table 3 Oxidation of 1,2-Diols

Entry	Diol	Time (h)	Product	Yield[a] (%)
1[b]		1		85
				10
2[c]		5		98
3[b]		3		52
				28
4[c]		3		99

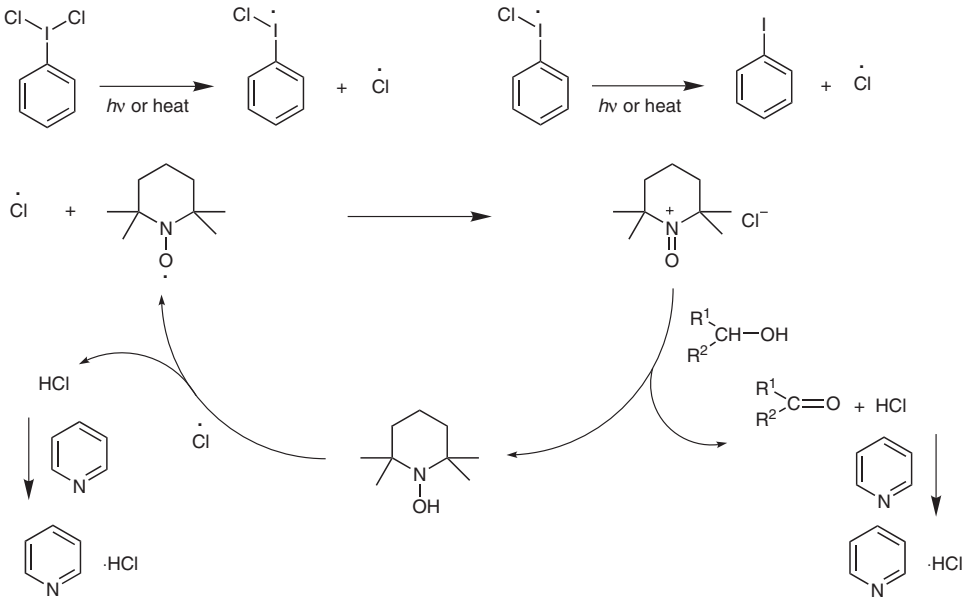
[a] Isolated yield.
[b] $PhICl_2$ (1.1 equiv), pyridine (2.2 equiv).
[c] $PhICl_2$ (3 equiv), pyridine (6 equiv).

cohols to the corresponding carbonyl compounds.[13] Since iodobenzene dichloride can decompose to release a chlorine atom upon light irradiation or heating,[14] we believed that TEMPO is oxidized to the oxoammonium salt by a chlorine atom that is generated by the homolytic breaking of the I–Cl bond in iodobenzene dichloride. Actually, the fact that the oxoammonium salt is generated by the oxidation of TEMPO by chlorine inspired us to propose that a chlorine atom oxidizes TEMPO to its oxoammonium salt.[15] Then, the oxoammonium salt oxidizes the alcohol to the corresponding carbonyl compound and is itself reduced to a hydroxylamine.[13] The second chlorine atom is thought to oxidize the hydroxylamine to TEMPO and the catalytic cycle is complete (Scheme 3).

Using the iodobenzene diacetate/TEMPO system,[12] 1,2-diols generate a five-membered ring intermediate after ligand exchange twice between iodobenzene diacetate and the 1,2-diol, which then collapses to give the cleavage products, aldehydes.[2a] However, in our oxidation system, the oxoammonium salt is thought to be the real oxidizing agent and it can oxidize 1,2-diols to α-hydroxy ketones or α-diketones smoothly without the formation of cleavage products.[16] This observation gives support to the proposed mechanism.

We also investigated methods for the preparation of iodoarene dichlorides. In 1886, Willgerodt developed the most commonly used method for the preparation of iodobenzene dichloride by passing a stream of chlorine gas into a solution of iodobenzene in chloroform at 0 °C.[1] The hazardous and inconvenient use of chlorine gas made the development of an efficient, safe, and convenient protocol for the preparation of iodobenzene dichloride from iodobenzene suitable for use in a synthetic laboratory desirable.

Mckillop et al. firstly described the preparation of iodobenzene dichloride by the oxidation of iodobenzene with sodium perborate in either acetonitrile or carbon tetrachloride in the presence of hydrochloric acid, but it was obtained in moderate yield only.[17] Thereafter, Skulski et

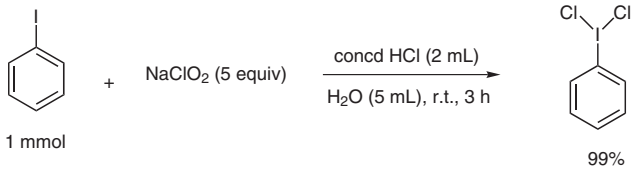


Scheme 3 Proposed mechanism

al. reported a number of new procedures for the preparation of iodoarene dichlorides in which chlorine was generated in situ by the reaction of aqueous hydrochloric acid with an appropriate oxidant such as potassium permanganate, activated manganese dioxide, potassium chlorate, sodium iodate trihydrate, concentrated nitric acid, sodium carbonate–hydrogen peroxide, sodium persulfate, chromium trioxide, and urea–hydrogen peroxide complex.[18a–i] These procedures have different shortcomings, such as complicated workup, use of toxic oxidants, high temperatures, and low yields for some substrates. We have developed two complementary procedures for the preparation of iodoarene dichlorides.

Sodium chlorite ($NaClO_2$) is a mild oxidant that has various applications in industry and synthetic organic chemistry. Our laboratory has recently developed a convenient method for the synthesis of epoxides from alkenes using sodium chlorite as the terminal oxidant without the use of a catalyst.[19] Starting from this work, we were interesting in exploring new reactivity of sodium chlorite. What we found was an efficient method for the preparation of iodoarene dichlorides from iodoarenes in dilute hydrochloric acid solution using sodium chlorite as an oxidant and acetonitrile as a co-solvent if necessary. The optimal reaction conditions are described in Scheme 4 with which iodobenzene could be oxidized to iodobenzene dichloride in 99% yield.

A wide range of iodoarenes were oxidized to their corresponding dichlorides in excellent yields (Table 4, entries 1–8). Both electron-withdrawing and electron-donating functional groups were tolerated under the reaction conditions. Notably, an iodoarene with a strong electron-donating group like 4-iodoanisole was oxidized to the corresponding dichloride in 92% yield (Table 4, entry 3). For 1-iodo-3-nitrobenzene and 1-iodo-4-nitrobenzene, the reaction rates were slow because of their poor solubility in water. This problem was overcome by the addition of acetonitrile (2 mL) as a co-solvent (Table 4, entry 9 vs 10 and entry 11 vs 12).



Scheme 4 Optimal reaction conditions for the preparation of iodobenzene dichloride by sodium chlorite

It has been reported that sodium chlorite reacts with hydrochloric acid to generate chlorine dioxide (ClO_2).[20] The reaction shown in Scheme 4 was monitored by UV spectroscopy and the characteristic peak of chlorine dioxide was observed. Moreover, chlorine dioxide was prepared according to a reported method; i.e., mixing of oxalic acid and potassium chlorate in water;[21] then it was passed into a suspension of iodobenzene in hydrochloric acid solution. After three hours, iodobenzene dichloride was obtained in 44% yield. Therefore, chlorine dioxide is believed to be the key agent in the chlorination of iodobenzene.

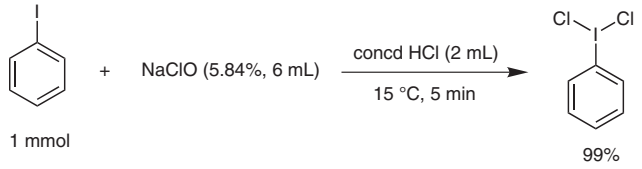
Sodium hypochlorite is a frequently used chlorine-based oxidant and it can react rapidly with hydrochloric acid to generate chlorine,[22] which could be used to chlorinate iodobenzene to give iodobenzene dichloride. As expected,

Table 4 Preparation of Iodoarene Dichlorides with Sodium Chlorite[a]

Entry	Substrate	Time (h)	Product	Yield (%)	Mp (°C)	Lit. mp (°C)
1	PhI	3	$PhICl_2$	99	111–113	111–112[18i]
2	4-MeC_6H_4I	11	4-$MeC_6H_4ICl_2$	99	97–98	97–98[18f]
3[b]	4-$MeOC_6H_4I$	2	4-$MeOC_6H_4ICl_2$	92	72–74	75–76[18i]
4	2-FC_6H_4I	8.5	2-$FC_6H_4ICl_2$	99	75–77	79–80[18i]
5	2-BrC_6H_4I	11.5	2-$BrC_6H_4ICl_2$	93	98–99	–
6	3-BrC_6H_4I	7	3-$BrC_6H_4ICl_2$	96	94–96	–
7	4-BrC_6H_4I	11.5	4-$BrC_6H_4ICl_2$	94	121–123	123–124[18b]
8	4-ClC_6H_4I	4	4-$ClC_6H_4ICl_2$	95	113–114	113–115[18i]
9	3-$O_2NC_6H_4I$	24	3-$O_2NC_6H_4ICl_2$	74	87	89–90[18b]
10[b]	3-$O_2NC_6H_4I$	6	3-$O_2NC_6H_4ICl_2$	94	–	–
11	4-$O_2NC_6H_4I$	24	4-$O_2NC_6H_4ICl_2$	63	172–174	175–176[18i]
12[b]	4-$O_2NC_6H_4I$	6	4-$O_2NC_6H_4ICl_2$	95	–	–

[a] Conditions: iodoarene (1 mmol), $NaClO_2$ (5 equiv), concd HCl (2 mL), H_2O (5 mL), r.t.
[b] MeCN (2 mL) was added as a co-solvent.

this was the case and sodium hypochlorite/hydrochloric acid brought about a drastic increase in the reaction rate compared with sodium chlorite/hydrochloric acid system since the preparation of iodobenzene dichloride from iodobenzene was complete in five minutes (Scheme 4 vs Scheme 5). The optimal reaction conditions are described in Scheme 5.



Scheme 5 Optimal reaction conditions for the preparation of iodobenzene dichloride by sodium hypochlorite

A number of iodoarenes were successfully chlorinated to their corresponding dichlorides in excellent yields and generally, these reactions proceeded at much faster reaction rate than that of the sodium chlorite/hydrochloric acid system (Table 5). It was worth indicating that 4-iodoanisole could not be oxidized to its dichloride using this protocol. Moreover, this method could be scaled up to 200 mmol of iodobenzene, producing 53 grams of iodobenzene dichloride after each run.

An efficient and mild alcohol oxidation method using iodobenzene dichloride as the stoichiometric oxidant catalyzed by TEMPO has been developed. 1,2-Diols could be oxidized to α-hydroxy ketones or α-diketones without the formation of the product of oxidative cleavage. Compared with other hypervalent iodine reagent based alcohol oxidation systems,[23] the oxidant, iodobenzene dichloride, used in our protocol is efficient and readily available since two convenient preparative procedures of iodobenzene dichloride are also reported. It is 120 years since the discovery of iodobenzene dichloride in the year of 1886, the new reactivity of iodobenzene dichloride reported here expands its synthetic application. Further studies on the synthetic utility of iodobenzene dichloride as an oxidizing reagent are underway in our laboratory.

$NaClO_2$ (80% purity), TEMPO, NaOCl (5.84%) were purchased from commercial suppliers and used without further purification. $CHCl_3$ and pyridine were distilled before use. The thermal stability of $PhICl_2$ is good; it could be stored at ca. 5 °C for >3 months without any change in its melting point and ^1H NMR spectrum. The known carbonyl products were identified by comparison of their ^1H and ^{13}C NMR spectrums with those reported in literature. The iodoarene dichlorides were identified by comparison to their literature melting points. The ^1H NMR spectra were recorded at 300 MHz or 400 MHz. and ^{13}C NMR spectra were measured at 75 MHz or 100 MHz, using $CDCl_3$ as the solvent.

Decanal; Typical Procedure

$PhICl_2$ (412.5 mg, 1.5 mmol) was added to a soln of decan-1-ol (158 mg, 1 mmol), TEMPO (12.5 mg, 0.08 mmol), and pyridine (0.26 mL, 3 mmol) in $CHCl_3$ (5 mL) at r.t. The reaction flask was placed in an oil bath at 50 °C and reaction was monitored by TLC. After 3 h, the mixture was cooled to r.t. and diluted with CH_2Cl_2 (50 mL). The resulting mixture was washed sequentially with sat. aq $Na_2S_2O_3$ (1 × 10 mL), 1 M HCl (1 × 10 mL), and brine (1 × 20 mL). The organic layer was dried (anhyd Na_2SO_4) and concentrated in vacuo to afford the crude product, which was purified to remove PhI and TEMPO by flash column chromatography (petroleum ether–EtOAc, 49:1) to give decanal as colorless oil; yield: 147 mg (94%).

Iodobenzene Dichloride Using Sodium Chlorite; Typical Procedure

$NaClO_2$ (566 mg, 5 mmol) was added portionwise over 10 min to a stirred soln of PhI (204 mg, 1 mmol) in dil HCl [made by mixing concd HCl (2 mL) and H_2O (5 mL)] at r.t. The mixture was stirred for 3 h. The resulting yellow precipitate was collected by filtration, washed with H_2O and light petroleum ether, and dried at r.t. in the dark overnight. The yellow solid was identified to be $PhICl_2$ by

Table 5 Preparation of Iodoarene Dichlorides with Sodium Hypochlorite[a]

Entry	Substrate	Time (min)	Product	Yield (%)	Mp (°C)	Lit. mp (°C)
1	PhI	5	$PhICl_2$	99	112–113	111–112[18i]
2	4-MeC_6H_4I	60	4-$MeC_6H_4ICl_2$	100	96–97	97-98[18f]
3	2-FC_6H_4I	45	2-$FC_6H_4ICl_2$	98	76–77	79–80[18i]
4	2-BrC_6H_4I	40	2-$BrC_6H_4ICl_2$	98	97–98	–
5	3-BrC_6H_4I	40	3-$BrC_6H_4ICl_2$	99	95–96	–
6[b]	4-BrC_6H_4I	60	4-$BrC_6H_4ICl_2$	96	121–122	123–124[18b]
7[b]	4-ClC_6H_4I	45	4-$ClC_6H_4ICl_2$	98	112–113	113–115[18i]
8[b]	3-$O_2NC_6H_4I$	40	3-$O_2NC_6H_4ICl_2$	98	90	89–90[18b]
9[b]	4-$O_2NC_6H_4I$	40	4-$O_2NC_6H_4ICl_2$	99	172–173	172–173[18i]
10[b]	4-PhC_6H_4I	80	4-$PhC_6H_4ICl_2$	94	85–87	85–87[18j]

[a] Conditions: iodoarene (1 mmol), 5.84% NaOCl (6 mL), concd HCl (2 mL), 15 °C.
[b] MeCN (2 mL) was used as a co-solvent.

comparison of its mp with that reported in the literature and its purity was 98.5% as determined by iodometric titration; yield: 272 mg (99%).

Iodobenzene Dichloride Using Sodium Hypochlorite; Typical Procedure

Concd HCl (2 mL) was added dropwise over 2 min to a stirring soln of iodobenzene (204 mg, 1 mmol) in aq 5.84% NaOCl soln (6 mL) at r.t. A yellow solid precipitated immediately and the reaction was complete after 5 min (TLC analysis). The resulting yellow solid was collected by filtration, washed with H_2O and light petroleum ether, and dried at r.t. in the dark overnight. The yellow solid was identified to be $PhICl_2$ by comparison of its mp with that reported in the literature. Its purity was 99% as determined by iodometric titration; yield: 271 mg (99%).

Iodobenzene Dichloride; Typical Large-Scale Procedure with Sodium Hypochlorite

Aq 5.84% NaOCl soln (800 mL) was added dropwise over 1 h to a vigorously stirred soln of iodobenzene (22.4 mL, 200 mmol) in concd HCl (200 mL) at r.t. Stirring was continued for a further 0.5 h when the addition of NaOCl was complete. The precipitated yellow solid was collected by filtration, washed with H_2O and light petroleum ether, and dried at r.t. in the dark overnight; yield: 52.9 g (96%).

Decanal (Table 2, Entry 1)[24]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1 H), 2.33–2.37 (m, 2 H), 1.52–1.57 (m, 2 H), 1.19–1.29 (m, 12 H), 0.81 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.73, 43.83, 31.77, 29.29, 29.17, 29.09, 22.57, 22.00, 13.99.

Octanal (Table 2, Entry 2)[25]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1 H), 2.33–2.36 (m, 2 H), 1.54–1.57 (m, 2 H), 1.21–1.23 (m, 8 H), 0.80 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.92, 43.89, 31.59, 29.09, 28.99, 22.56, 22.05, 14.02.

Hexadecanal (Table 2, Entry 3)[26]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1 H), 2.33–2.37 (m, 2 H), 1.53–1.57 (m, 2 H), 1.18–1.22 (m, 24 H), 0.81 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.84, 43.88, 31.90, 29.64, 29.33, 29.14, 22.66, 22.05, 14.09.

Octan-2-one (Table 2, Entry 4)[27]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33–2.37 (m, 2 H), 2.06 (s, 3 H), 1.46–1.51 (m, 2 H), 1.18–1.25 (m, 6 H), 0.82 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.24, 43.71, 31.51, 29.74, 28.76, 23.73, 23.41, 13.93.

Menthone (Table 2, Entry 5)[28]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26–2.30 (m, 1 H), 1.82–2.06 (m, 6 H), 1.27–1.30 (m, 2 H), 0.93 (d, *J* = 6.4 Hz, 3 H), 0.84 (d, *J* = 7.2 Hz, 3 H), 0.78 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.17, 55.69, 50.72, 35.34, 33.78, 27.17, 25.73, 22.16, 21.08, 18.55.

Acetophenone (Table 2, Entry 6)[27]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.88 (m, 2 H), 7.46–7.50 (m, 1 H), 7.36–7.39 (m, 2 H), 2.52 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.07, 136.96, 133.02, 128.47, 128.20, 26.56.

(2*Z*)-4-(Tetrahydropyran-2-yloxy)but-2-enal (Table 2, Entry 8)[29]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (d, *J* = 8 Hz, 1 H), 6.79–6.85 (m, 1 H), 6.30–6.36 (m, 1 H), 4.62 (t, 1 H), 4.43–4.49 (m, 1 H), 4.17–4.22 (m, 1 H), 3.76 (t, *J* = 7.2 Hz, 1 H), 3.45–3.48 (m, 1 H), 1.48–1.77 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.36, 153.39, 131.42, 98.25, 65.44, 62.04, 30.24, 25.22, 19.02.

2-Hydroxycyclooctan-1-one (Table 3, Entry 1)[30]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (t, *J* = 7.2 Hz, 1 H), 3.73 (s, 1 H), 2.71–2.72 (m, 1 H), 2.34–2.35 (m, 2 H), 1.95–2.05 (m, 2 H), 1.59–1.81 (m, 4 H), 1.37–1.39 (m, 2 H), 0.88–0.92 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 217.38, 75.99, 37.07, 29.13, 28.38, 25.27, 24.25, 21.90.

Cyclooctane-1,2-dione (Table 3, Entry 2)[31]

^{1}H NMR (400 MHz, $CDCl_3$): 2.51–2.54 (t, *J* = 7.2 Hz, 4 H), 1.72–1.73 (m, 4 H), 1.56–1.58 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.05, 29.93, 26.33, 21.11.

Benzoin (Table 3, Entry 3)[32]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.91 (d, *J* = 7.2 Hz, 2 H), 7.48–7.51 (m, 1 H), 7.24–7.39 (m, 7 H), 5.95 (d, *J* = 6 Hz, 1 H), 4.58 (d, *J* = 6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.85, 138.90, 133.85, 133.36, 129.07, 128.62, 128.50, 127.70, 76.14.

Benzil (Table 3, Entry 4)[33]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8 Hz, 4 H), 7.66–7.68 (m, 2 H), 7.50–7.54 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.51, 134.83, 132.82, 129.78, 128.93.

Acknowledgment

This work was financially supported by The National Natural Science Foundation of China (No. 20572046 and No. 20421202), the 111 Project (B06005), and the Ministry of Education of China.

References

(1) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 154.
(2) (a) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243. (b) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123. (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523. (d) Zanka, A.; Takeuchi, H.; Kubota, A. *Org. Process Res. Dev.* **1998**, *2*, 270. (e) Ibrahim, H.; Kleinbeck, F.; Togni, A. *Helv. Chim. Acta* **2004**, *87*, 605.
(3) Garvey, B. S.; Halley, L. F. Jr.; Allen, C. F. H. *J. Am. Chem. Soc.* **1937**, *59*, 1827.
(4) (a) White, P.; Breslow, R. *J. Am. Chem. Soc.* **1990**, *112*, 6842. (b) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.
(5) (a) Bennett, M. A.; Bhargava, S. K.; Bond, A. M.; Edwards, A. J.; Guo, S.-X.; Privér, S. H.; Rae, A. D.; Willis, A. C. *Inorg. Chem.* **2004**, *43*, 7752. (b) Hayton, T. W.; Legzdins, P.; Patrick, B. O. *Inorg. Chem.* **2002**, *41*, 5388. (c) Bhargava, S. K.; Mohr, F.; Bennett, M. A.; Welling, L. L.; Willis, A. C. *Organometallics* **2000**, *19*, 5628. (d) Witte, P. T.; Meetsma, A.; Hessen, B. *Organometallics* **1999**, *18*, 2944. (e) Filippou, A. C.; Winter, J. G.; Kociok-Kohn, G.; Troll, C.; Hinz, I. *Organometallics* **1999**, *18*, 2649.

(6) (a) Prakash, O.; Rani, N.; Sharma, V.; Moriarty, R. M. *Synlett* **1997**, 1255. (b) Prakash, O.; Kaur, H.; Batra, H.; Rani, N.; Singh, S. P.; Moriarty, R. M. *J. Org. Chem.* **2001**, *66*, 2019.
(7) Prakash, O.; Sharma, V.; Batra, H.; Moriarty, R. M. *Tetrahedron Lett.* **2001**, *42*, 553.
(8) Kita, Y.; Takeda, Y.; Okuno, T.; Egi, M.; Iio, K.; Kawaguchi, K.-I.; Akai, S. *Chem. Pharm. Bull.* **1997**, *45*, 1887.
(9) Radhakrishna, A. S.; Sivaprakash, K.; Singh, B. B. *Synth. Commun.* **1991**, *21*, 1625.
(10) Radhakrishna, A. S.; Augustine, B.; Sivaprakash, K.; Singh, B. B. *Synth. Commun.* **1991**, *21*, 1473.
(11) Wicha, J.; Zarecki, A.; Kocór, M. *Tetrahedron Lett.* **1973**, *14*, 3635.
(12) De Mico, A.; Margarita, R.; Parlanti, L.; Vescovi, A.; Piancatelli, G. *J. Org. Chem.* **1997**, *62*, 6974.
(13) For two recent reviews, see: (a) De Nooy, A. E. J.; Besemer, A. C.; Van Bekkum, H. *Synthesis* **1996**, 1153. (b) Sheldon, R. A.; Arends, I. W. C. E. *Adv. Synth. Catal.* **2004**, *346*, 1051. For the NCS/TEMPO system, see: (c) Einhorn, J.; Einhorn, C.; Ratajczak, F.; Pierre, J.-L. *J. Org. Chem.* **1996**, *61*, 7452. For the 1,3,5-trichloro-2,4,6-triazinetrione/ TEMPO system, see: (d) De Luca, L.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2001**, *3*, 3041. For TEMPO with metal complexes as co-catalyst aerobic oxidation systems, see: (e) Gamez, P.; Arends, I. W. C. E.; Sheldon, R. A.; Reedijk, J. *Adv. Synth. Catal.* **2004**, *346*, 805. (f) Velusamy, S.; Srinivasan, A.; Punniyamurthy, T. *Tetrahedron Lett.* **2006**, *47*, 923. For the TEMPO/$NaNO_2$/ 1,3-dibromo-5,5-dimethylhydantoin protocol, see: (g) Liu, R.; Dong, C.; Liang, X.; Wang, X.; Hu, X. *J. Org. Chem.* **2005**, *70*, 729. For metal-free TEMPO-catalyzed aerobic oxidation systems, see: (h) Liu, R.; Liang, X.; Dong, C.; Hu, X. *J. Am. Chem. Soc.* **2004**, *126*, 4112. (i) Herrerías, C. I.; Zhang, T. Y.; Li, C.-J. *Tetrahedron Lett.* **2006**, *47*, 13.
(14) (a) Banks, D. F.; Huyeser, E. F.; Kleinberg, J. *J. Org. Chem.* **1964**, *29*, 3692. (b) Igarashi, K.; Honma, T. *J. Org. Chem.* **1970**, *35*, 617. (c) Tanner, D. D.; Van Bostelen, P. B. *J. Org. Chem.* **1967**, *32*, 1517.
(15) (a) Hunder, D. H.; Barton, D. H. R.; Motherwell, W. J. *Tetrahedron Lett.* **1984**, *25*, 603. (b) Hunter, D. H.; Racok, J. S.; Rey, A. W.; Zea-Ponce, Y. *J. Org. Chem.* **1988**, *53*, 1278.
(16) (a) Miyazawa, T.; Endo, T. *J. Org. Chem.* **1985**, *50*, 3930. (b) Banwell, M. G.; Bridges, V. S.; Dupuche, J. R.; Richards, S. L.; Walter, J. M. *J. Org. Chem.* **1994**, *59*, 6338.
(17) Koyuncun, D.; Mckillop, A.; Mclaren, L. *J. Chem. Res., Synop.* **1990**, 21.
(18) (a) Kaimierczak, P.; Skulski, L.; Obeid, N. *J. Chem. Res., Synop.* **1999**, 64. (b) Krassowska-Swiebocka, B.; Prokopienko, G.; Skulski, L. *Synlett* **1999**, 1409. (c) Obeid, N.; Skulski, L. *Polish J. Chem.* **2000**, *74*, 1609. (d) Baranowski, A.; Plachta, D.; Skulski, L.; Klimaszewska, M. *J. Chem. Res., Synop.* **2000**, 435. (e) Skulski, L. *Molecules* **2000**, *5*, 1331. (f) Obeid, N.; Skulski, L. *Molecules* **2001**, *6*, 869. (g) Lulinski, P.; Obeid, N.; Skulski, L. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2433. (h) Skulski, L. *Molecules* **2003**, *8*, 45. (i) Zielinska, A.; Skulski, L. *Tetrahedron Lett.* **2004**, *45*, 1087. (j) Remarkably, A.; Ranganathan, D.; Pamachandran, P. V. *Tetrahedron* **1984**, *40*, 3145.
(19) Geng, X. L.; Wang, Z.; Li, X.-Q.; Zhang, C. *J. Org. Chem.* **2005**, *70*, 9610.
(20) Lore, B. *Gas- Wasserfach* **1965**, *106*, 783.
(21) Dunn, R. C.; Simon, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 4856.
(22) George, C. *Sch. Sci. Rev.* **1973**, *54*, 533.
(23) Tohma, H.; Kita, Y. *Adv. Synth. Catal.* **2004**, *346*, 111.
(24) Jiang, N.; Ragauskas, A. J. *Org. Lett.* **2005**, *7*, 3689.
(25) Anderson, C. D.; Shea, K. J.; Rychnovsky, S. D. *Org. Lett.* **2005**, *7*, 4879.
(26) Taber, D. F.; Amedio, J. C. Jr.; Jung, K. *J. Org. Chem.* **1987**, *52*, 5621.
(27) Miranda, P. O.; Diaz, D. D.; Padron, J. I.; Ramirez, M. A.; Martin, V. S. *J. Org. Chem.* **2005**, *70*, 57.
(28) Gonzalez-Nunez, M. E.; Mello, R.; Olmos, A.; Acerete, R.; Asensio, G. *J. Org. Chem.* **2006**, *71*, 1039.
(29) Toshio, N.; Mitsuo, N.; Keiichi, O. *Chem. Pharm. Bull.* **1987**, *35*, 2635.
(30) Chai, W.; Takeda, A.; Hara, M.; Ji, S.; Horiuchi, C. A. *Tetrahedron* **2005**, *61*, 2453.
(31) Amon, C. M.; Banwell, M. G.; Gravatt, G. L. *J. Org. Chem.* **1987**, *52*, 4851.
(32) Plietker, B. *J. Org. Chem.* **2004**, *69*, 8287.
(33) Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 4852.