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Facile, Efficient, and Environmentally Friendly α- and Aromatic Regioselective Chlorination of Toluene using $KHSO_5$ and KCl under Catalyst-free Conditions

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Toluene was subjected to room-temperature chlorination with the $KHSO_5$/KCl system in organic solvent-water mixtures. In a typical reaction, the amounts of toluene, $KHSO_5$, and KCl were 1.0, 5.0 and 7.5 millimoles, respectively. The reaction mixtures, consisting of an organic solvent (2.50 mL) and water (1.50 mL), were rather multiphase like slurry. Depending on the nature of the organic solvent present in the solvent mixtures, either α-chlorination or aromatic chlorination of toluene was favoured. The chlorinated solvents CH_2Cl_2, $CHCl_3$, and CCl_4 favoured the α-chlorination, yielding >81% benzyl chloride selectivity in 38-59% toluene conversions in 1 hour. The water miscible polar solvents C_2H_5OH, CH_3OH, and CH_3CN favoured the aromatic chlorination, yielding 61-86% chlorotoluene selectivity in >98% toluene conversions in 1 hour. Reactions carried out in all solvent mixtures yielded only chlorinated toluene products. The method presented here for the regioselective chlorination of toluene meets the goals of green chemistry as well in a number of ways: a. Catalyst-free conditions; b. Nontoxic, green, safe, stable, and inexpensive reagents; c. Low environmental impact; d. No heating or cooling; e. Simple and cheap operation; and f. High regioselectivity.

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Introduction

α- and aromatic regioselective halogenations of alkyl aromatics are important reactions in the production of bulk and fine chemicals for both industrial and laboratory use.[1,2] Such transformations lead to the production of versatile, valuable starting materials for many applications. Many α- and aromatic halogenation reactions of alkyl aromatics with various halogenation reagents, oxidants, and catalysts under different reaction conditions have been reported in the literature. However, most of these reactions suffer from low yield, low regioselectivity, long reaction times, require hazardous reagents, employ catalysts which are expensive and hard to prepare, and involve handling problems.[1,3-25] The halogenation of alkyl aromatics usually favours aromatic (ring) halogenated products via electrophilic substitution.[1,3-23,26] On the other hand the α-halogenation of alkyl aromatics proceeds via free radical mechanisms and few papers have reported such regioselective halogenations.[12,14,23,24]

Aromatic and α-chlorinations or other halogenations of toluene have been the subject of much lab-scale research. Aromatic chlorination of toluene was achieved with the iron(III) chloride-crown ether complexes,[6] sodium chlorite-trichloroacetic acid mixtures in CH_2Cl_2,[12] N-chlorinated amines and N-chlorinated ammonium salts in trifluoroacetic acid at room temperature,[13] SO_2Cl_2/zeolite systems,[16,18] kaolinitic clay catalyzed Cl_2 and SO_2Cl_2,[19] the KCl/Oxone system in CH_3CN and in a 3:1 (v/v) H_2O-CH_3CN mixture at room temperature.[1,20] Recently, the solvent-free aromatic chlorination and bromination of toluene along with certain alkyl aromatics in a mixer ball mill using Oxone and NaX (X=Cl, Br) in the presence of several milling auxiliaries has been described.[26] Furthermore, successful aromatic bromination or iodination of toluene has been reported with the NaBr or NaI/cerium(III) chloride/H_2O_2 catalyst-oxidant system in water at room temperature under reflux conditions.[7] In addition, the Br_2/SO_2Cl_2/zeolite catalytic system at 25 °C resulted in aromatic brominated toluene.[15]

In addition, there have been few reports regarding the α-chlorination of toluene in the literature. Muathen obtained benzyl chloride along with o-chlorotoluene and p-chlorotoluene from toluene using sodium chlorite-trichloroacetic acid mixtures in CH_2Cl_2.[12] It seems that sodium chlorite-trichloroacetic acid mixtures produce the chlorinating agent, chlorous acid, *in situ*. By changing the molar ratios of toluene, chlorous acid and trichloroacetic acid from 1:3:6 to 1:3:3, the author was able to alter the yields of benzyl chloride (from 20% to 65%) and of aromatic chlorinated products (from 80% to 35%). This study shows that changing the composition of the components in the reaction mixtures alters the dominant reaction path, in other words, the reaction mechanism. Fonouni et al. demonstrated a high-yield conversion of toluene to benzyl chloride using hypochlorite, sodium chloride and a PTC (tetrabutylammonium hydrogen sulfate) in H_2O (pH 8.5)-CH_2Cl_2 mixtures at 22 °C in 90 minutes.[24] It was found that 94% of toluene reacted and 64% (based on consumed toluene) benzyl chloride was obtained. Minor products were aromatic

chlorination and oxidation products of toluene with the most significant being benzal chloride with an 11% yield. Furthermore, a bromination attempt for toluene with NBS under UV radiation in CH_3CN at 30 °C resulted in a 76% conversion and 100% benzyl bromide selectivity in 15 minutes, and a 95% conversion and 95% selectivity in 30 minutes.[14] The same bromination reaction carried out with the brominating reagents NBS and HBr-H_2O_2 under a 40 W incandescent light in water at room temperature resulted in a 84% benzyl bromide yield in 25 hours and a 79% yield in 10 hours, respectively.[23] The chlorinated products of toluene, such as benzyl chloride, benzal chloride, o-chlorotoluene, and p-chlorotoluene are industrially-important compounds utilized in broad applications. Among them, benzyl chloride is the most economically significant. However, industrial production processes of chlorinated toluenes are not environmentally friendly.[27]

Oxone is an attractive oxidant due to its nontoxic, green and safe nature, its stability, and affordability and its frequent use in synthetic chemistry applications.[28] It is a triple salt of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, and potassium peroxymonosulfate ($KHSO_5$) is its active component. Oxone has been employed in the halogenation reactions of toluene and certain alkyl aromatics.[1,20-22] These reactions produced corresponding aromatic halogenated products.

In this study, we achieved α- and aromatic chlorination of toluene in high regioselectivity using the environmentally benign, cheap, readily available reagents, $KHSO_5$ and potassium chloride without the use of any catalyst in water-organic solvent mixtures.

Results and discussion

Regioselective chlorination of toluene with $KHSO_5$ and KCl

Toluene, also a model compound for alkyl aromatics, was subjected to room-temperature chlorination achieved with the $KHSO_5$/KCl system in organic solvent-water mixtures. $KHSO_5$ was introduced into the reaction medium as Oxone, a triple salt of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Either the radical chlorination mechanism or the electrophilic chlorination mechanism was predominantly favoured, dependent solely on the nature of the organic solvent present in the solvent mixtures. The reactions run in all solvent mixtures yielded only chlorinated toluene products (the formation of any oxygen containing product was not indicated by the GC-MS library). Furthermore, the reactions did not proceed in the absence of any of $KHSO_5$ and KCl.

Effect of the organic solvent in the mixtures

We screened CH_2Cl_2, $CHCl_3$, and CCl_4 as water immiscible co-solvents and CH_3OH, C_2H_5OH, and CH_3CN as water miscible, polar co-solvents in organic solvent-water mixtures in the chlorination of toluene with the $KHSO_5$/KCl system. The reaction media are rather multiphase mixtures like slurry when they consist of one of the organic solvents (2.50 mL), water

(1.50 mL), and undissolved portions of Oxone and KCl. The amounts of Oxone and KCl used were *ca.* 3.4 and 1.1 times the amounts that can be dissolved in 1.50 mL of water, respectively.

A radical mechanism in the chlorination reaction was favoured leaving benzyl chloride as the major product in the presence of the chlorinated organic solvents CH_2Cl_2, $CHCl_3$, and CCl_4 (entry 1-3, Table 1). The conversions of toluene were 38-59% in 1 hour with the benzyl chloride regioselectivity being remarkably high (above 80%) for these solvents. It should be noted that the conversion of toluene in the commercial benzyl chloride production process is kept at less than 50% in order to maximize benzyl chloride selectivity and to minimize the extent of the other methyl group chlorinated products.[29] It should also be noted that we observed extensive gas evolution over the duration of these reactions. A gas test was positive for Cl_2 because it turned moist litmus paper from blue to red, after which the paper was bleached white. In the literature, there are reports regarding the formation of the chlorine radical ($Cl^·$) and molecular chlorine (Cl_2) when chloride ions are treated with Oxone.[30-33] We also checked the pH values of the aqueous phase of a reaction mixture before and after the reaction and found 4.45 and 3.83, respectively. When we carried out a reaction whose medium was buffered with acetic acid/sodium acetate at pH 4.45 gave higher toluene conversion (80%) but poorer benzyl chloride yield (28%) compared to those obtained for the standard reaction.

Aside from our $Cl^·$ radical and molecular Cl_2 generation course, Oxone was usually activated with transitional metal ions, their complexes, UV or visible light in order to oxidize the Cl^- ion. In our study, we did not attempt to activate Oxone deliberately, except the reactions were carried out in daylight. In fact, we did not observe significant change in the outcome of the chlorination reaction of toluene in a control experiment run in darkness. Meanwhile, Cl_2 gas evolution was observed even when the solvent was only water in the presence of toluene, as well as in the chlorinated solvent-water mixtures and in water alone in the absence of toluene.

With only the solvent CH_2Cl_2, the conversion of toluene was about 3% and no benzyl chloride formation was observed (entry 4, Table 1). This result may be attributed to the insolubility of Oxone and KCl in the reaction medium and, or not, to the formation of active chlorinating species in CH_2Cl_2. Moreover, the reaction did not proceed well when the solvent H_2O was replaced with C_2H_5OH in the CH_2Cl_2-H_2O mixture (entry 5, Table 1). On the other hand, the reaction went to completion when the solvent was H_2O, although the majority of the products were two or more chlorinated products of toluene (entry 6, Table 1). These observations lead us to believe that the presence of a certain amount of water with the chlorinated co-solvent is crucial for the formation of active chlorinating species in the medium. A similar finding was reported for dichlorination of allylic and homoallylic alcohol derivatives.[33] We also observed that the $KHSO_5$/KCl system was able to chlorinate the co-solvent CH_2Cl_2 to $CHCl_3$ in the absence of toluene in the CH_2Cl_2-H_2O mixture.
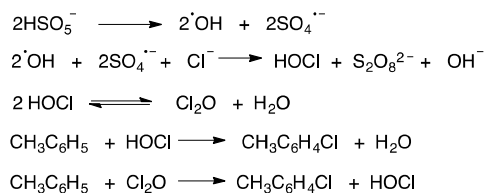
In the presence of the highly polar (water miscible) co-solvents CH_3OH, C_2H_5OH, and CH_3CN with water in the chlorination medium, the conversion of toluene to some of its chlorinated products was nearly quantitative, but here, a electrophilic chlorination mechanism rather than a radical mechanism operated. The major chlorination products were *o*-chlorotoluene and *p*-chlorotoluene although substantial amounts of two or more chlorine containing products were also formed (entry 7-9, Table 1). No α-chlorination product was observed in these reactions. Contrary to chlorinated solvent-water mixture cases, the evolution of Cl_2 gas was not evidenced in the CH_3OH-, C_2H_5OH-, and CH_3CN-water mixtures presenting further proof that a different chlorination mechanism is acting in these solvent mixtures. CH_3OH and C_2H_5OH are good radical quenchers and they apparently quenched any radical species as soon as they formed (or if they formed), and thus, the radical mechanism pathway was blocked. CH_3CN seemingly acts in the same way as alcohols. Among the co-solvents, CH_3OH, C_2H_5OH, and CH_3CN, the best toluene chlorination results, in terms the conversion of toluene (98%) and selectivity for mono aromatic chlorinated products (86%), were achieved in the presence of C_2H_5OH (entry 7, Table 1).

The screening of the solvent mixtures reveals that both the percentages of the chlorination of toluene, and of the regioselectivity of the chlorine atom on it, can be controlled to a large extent, simply by changing the type of organic solvent in the mixture. As mentioned earlier, α- and aromatic regioselective compounds are industrially important and versatile compounds in the production of functional and fine chemicals. The $KHSO_5$/KCl chlorination system employed here gives a versatile and facile way to synthesize either type of regioselective compound. In addition, the results for the regioselective chlorination of toluene obtained simply by changing the organic constituent of the solvent mixture are noteworthy.

Because the conversion of toluene to chlorinated products in C_2H_5OH-, CH_3OH-, and CH_3CN-H_2O mixtures was nearly quantitative and the chlorotoluene regioselectivities were high (entry 7-9, Table 1), we did not further study the aromatic chlorination reaction of toluene with the $KHSO_5$/KCl system. The aromatic chlorination mechanism of toluene adapted from literature is given in Scheme 1.[1,21,26] In this mechanism, the decomposition products of HSO_5^- react with Cl^- to produce HOCl which may convert into Cl_2O.[34] Both species are known active chlorinating species. Then HOCl or Cl_2O reacts with toluene via electrophilic mechanism to afford the aromatic chlorinated product monochlorotoluene. Beyond this point, we devoted our efforts to investigating in detail the α-chlorination of toluene with the $KHSO_5$/KCl system in CH_2Cl_2-H_2O mixtures.

Scheme 1. A Plausible Mechanism for Aromatic Chlorination

$$2HSO_5^- \longrightarrow 2^·OH + 2SO_4^{·-}$$
$$2^·OH + 2SO_4^{·-} + Cl^- \longrightarrow HOCl + S_2O_8^{2-} + OH^-$$
$$2HOCl \rightleftharpoons Cl_2O + H_2O$$
$$CH_3C_6H_5 + HOCl \longrightarrow CH_3C_6H_4Cl + H_2O$$
$$CH_3C_6H_5 + Cl_2O \longrightarrow CH_3C_6H_4Cl + HOCl$$

Table 1. Effect of the Reaction Medium in the Chlorination of Toluene[a]

Entry	Medium	Conversion (%)	BzCl[b] (%)	ClTol[c] (%)	Other products[d] (%)	BzCl[b] Selectivity (%)	ClTol[c] Selectivity (%)
1	CH_2Cl_2-H_2O	59	48	<2	10	81	
2	$CHCl_3$-H_2O	38	33	<2	4	87	
3	CCl_4-H_2O	43	38	<2	4	86	
4	CH_2Cl_2	3	0	0	3		
5	CH_2Cl_2-C_2H_5OH[e]	4	0	0	0		
6	H_2O	100	21	4	75	21	
7	C_2H_5OH-H_2O	98	0	84 (55 (oCT), 29 (pCT))	14		86
8	CH_3OH-H_2O	100	0	62 (41 (oCT), 21 (pCT))	38		62
9	CH_3CN-H_2O	99	0	61 (34 (oCT), 27 (pCT))	39		61

[a] Toluene=1.0 mmol, $KHSO_5$=5.0 mmol (Oxone=2.5 mmol), KCl=7.5 mmol, Organic solvent=2.50 mL, H_2O=1.50 mL, t=1 h, room temperature. [b] Benzyl chloride, [c] Chlorotoluene (oCT: o-chlorotoluene, pCT: p-chlorotoluene), [d] Two or more chlorine containing toluene derivatives. [e] The reaction product unidentified.

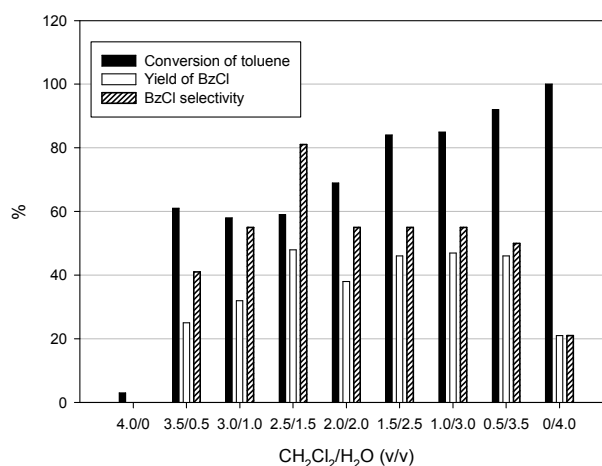### Effect of the CH_2Cl_2-H_2O solvent composition

Figure 1 gives the percentages of the conversion of toluene into its chlorinated products and of the selectivity for benzyl chloride in varying the CH_2Cl_2-H_2O mixture compositions. It is clear that the mixture composition affected both toluene conversion and benzyl chloride selectivity. As the amount of H_2O increased (while the amount of CH_2Cl_2 decreased, keeping a total mixture of volume 4.00 mL) in the mixtures, the percentage of conversion of toluene increased as a whole. Meanwhile, the highest benzyl chloride selectivity, ranging from 55% to 81%, was obtained in mixtures containing 1.00-3.00 mL CH_2Cl_2. The best selectivity for benzyl chloride (81%) was obtained in the 2.50/1.50 (v/v) CH_2Cl_2/H_2O ratio. In conclusion, the higher H_2O content in the solvent mixtures led to higher toluene conversion, but the selectivity of benzyl chloride was not maintained in accordance with the conversion of toluene. It appears that a solvent mixture of 2.50 mL CH_2Cl_2-1.50 mL H_2O yields optimal toluene conversion and benzyl chloride selectivity values (entry 1, Table 1 and Figure 1). Thereafter, we employed this solvent mixture composition to investigate the effects of time and the amounts of toluene, $KHSO_5$, and KCl on the chlorination of toluene.

Effect of the reaction time

Figure 2 shows the time dependence of the percentages of the conversion of toluene, and of the yield of benzyl chloride in the chlorination of toluene with the $KHSO_5$/KCl system under our standard reaction conditions. The conversion of toluene and the yield of benzyl chloride increased quickly with an increase in reaction time for the first ca. 1 hour reaching values of approximately 59% and 48%, respectively. Thereafter, they almost levelled off. After 5 hours, the conversion of toluene was 71%, with the yield of benzyl chloride at 57%.

From the reaction profile (Figure 2), it can be deduced that the reaction slowed down after 1 hour and could not continue to completion. Because severe Cl_2 gas evolution during the reaction also consumes the reagents $KHSO_5$ and KCl, we investigated whether the depletion of $KHSO_5$ and/or KCl was the reason for the slowdown in reaction. The addition of 7.5 mmol KCl more to the standard reaction medium after a 1 hour

reaction period resulted in only a ca. 2% increase in the conversion of toluene, but a 5% decrease in the yield of benzyl chloride in the following one hour reaction period. Likewise the addition of 5.0 mmol $KHSO_5$ more to the standard reaction medium after a 1 hour reaction period resulted in only a 13% increase in the conversion of toluene and a ca. 2% decrease in the yield of benzyl chloride in the following one hour reaction period. When both reagents $KHSO_5$ (5.0 mmol) and KCl (7.5 mmol) were added to the standard reaction medium after a 1 hour reaction period, the conversion of toluene increased by 34% (from 59% to 93%) and the yield of benzyl chloride increased by ca. 1% (from 48% to 49%) in the following one hour reaction period. These findings show that the addition of $KHSO_5$ and/or KCl, apart from improvement, decreased the yield and selectivity of benzyl chloride causing further chlorination of benzyl chloride. Although we did not attempt to fully identify or quantify these further chlorination products of benzyl chloride some, such as benzal chloride, are also industrially valuable starting materials.

Figure 1. Effect of the composition of CH_2Cl_2-H_2O mixtures on the conversion of toluene and the yield and selectivity of benzyl chloride Conditions: Toluene=1.0 mmol, $KHSO_5$=5.0 mmol, KCl=7.5 mmol, total volume of CH_2Cl_2 and H_2O=4.00 mL, reaction time1 hour, at room temperature.
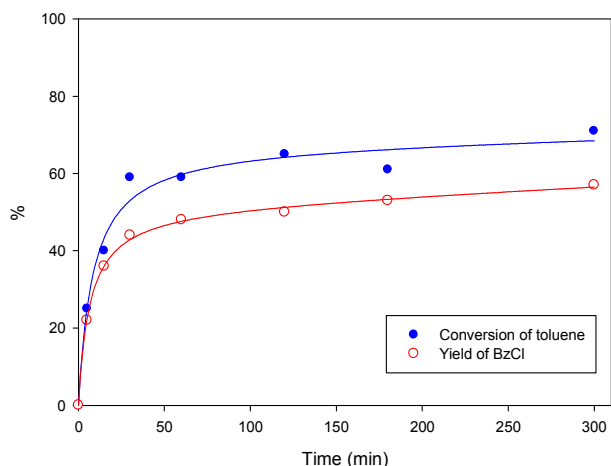
Figure 2. Percentages of the conversion of toluene and yield of benzyl chloride against time in the chlorination of toluene

Conditions: Toluene=1.0 mmol, $KHSO_5$=5.0 mmol, KCl=7.5 mmol, CH_2Cl_2=2.50 mL, H_2O=1.50 mL, reaction time1 hour, at room temperature.

Effect of the amount of KCl, $KHSO_5$, and toluene

In Table 2, entry 1 is the standard reaction employed in comparisons. We observed that a variation in the amount of KCl had a great effect on the conversion of toluene and the yield of benzyl chloride. By decreasing the amount of KCl by a third, sharp decreases were observed on the conversion of toluene and the yield of benzyl chloride (entry 2, Table 2). In contrast, increasing the amount of KCl by a third resulted in a significant rise in the conversion of toluene together with a slight decrease in yield of benzyl chloride and, eventually, a substantial decrease in benzyl chloride selectivity occurred (entry 3, Table 2). Here, the amount of over-chlorinated products with respect to that of benzyl chloride became important. When the amount of $KHSO_5$ was decreased by one half of 5.0 mmol, the percentages of the conversion of toluene and of the yield of benzyl chloride remained almost the same as those in the standard reaction (entry 4, Table 2). On the other hand, increasing the amount of $KHSO_5$ by 50% (from 5.0 mmol to 7.5 mmol) dramatically reduced both the conversion of toluene and the yield of benzyl chloride (entry 5, Table 2). It appears that the amounts of and the ratio of KCl and $KHSO_5$ should be kept in relative balance where KCl should be approximately 50% more than $KHSO_5$ in order to achieve high benzyl chloride yield and selectivity. When both reagents were in equal quantities, the conversion of toluene dropped significantly (entries 2 and 5, Table 2). When the amount of toluene was doubled (entry 6, Table 2), the amounts of converted toluene (0.74 mmol) and of benzyl chloride (0.58 mmol) were higher than those obtained under standard conditions (0.59 mmol and 0.48 mmol, respectively), although 1.24 mmol (62%) of the starting toluene remained unreacted. Furthermore, the benzyl chloride selectivity was also comparable for both reactions.

Table 2. Effects of the amount of KCl, $KHSO_5$, and toluene in the chlorination of toluene

Entry	Toluene (mmol)	$KHSO_5$ (mmol)	KCl (mmol)	Conversion (%)	BzCl yield (%)	BzCl selectivity (%)
1	1.0	5.0	7.5	59	48	81
2	1.0	5.0	5.0	20	17	85
3	1.0	5.0	10.0	92	46	50
4	1.0	2.5	7.5	60	46	77
5	1.0	7.5	7.5	16	12	75
6	2.0	5.0	7.5	37	29	78

CH_2Cl_2=2.50 mL, H_2O=1.50 mL, reaction time 1 hour, at room temperature

α-Chlorination mechanism of toluene

A plausible mechanism for the α-chlorination of toluene with the $KHSO_5$/KCl system in chlorinated solvent-H_2O mixtures is given in Scheme 2. The proposed mechanism is a radical mechanism. The generation of the chlorine radicals in our $KHSO_5$/KCl system is the most intriguing part of the chlorination process of toluene and the reaction conditions apparently produce free chlorine molecules and chlorine radicals from the $KHSO_5$-KCl couple efficiently. The formation of chlorine molecules occurs in two steps: HSO_5^- and Cl^- react to give HOCl in the first step. HOCl reacts further with HCl (Cl^- ions in acidic reaction medium) to produce Cl_2 molecules.[35] However the formation route of chlorine radicals is not clear for us. They may form from the bond breaking reaction of Cl_2 molecules or from the oxidation of Cl^- ions with the $SO_4^{\cdot-}$ radicals or $\cdot$OH radicals. Both are the decomposition products of HSO_5^-.[36] Once a chlorine radical is generated in the reaction, it abstracts one of the methyl group hydrogens of toluene and the benzyl radical forms. This radical either combines with another chlorine radical (Route 1) or reacts with a free chlorine molecule to give the product benzyl chloride (Route 2). A recent detailed review regarding the application of Oxone in synthetic chemistry did not cite any research paper that applies similar reaction conditions developed in this study to synthesize a benzyl chlorinated compound.[37] However, two research papers in the literature report the use of the $KHSO_5$/KBr system in CH_2Cl_2-H_2O mixtures for direct benzylic oxidation of certain alkylarenes[32], and the $KHSO_5$/Cl^- system in CH_2Cl_2-H_2O mixtures for diastereoselective chlorination of allylic and

homoallylic derivatives.[33] The reaction media in both studies were CH_2Cl_2-H_2O mixtures like our own, but with products in a broad range of carbonyl compounds and those of dichlorination of allylic double bond. Therefore, we propose that our chlorination procedure is a new synthetic route to chlorinate toluene and alkyl aromatics and perhaps even other substances via the radical chlorination mechanism.

Scheme 2. A Plausible Mechanism for α-Chlorination
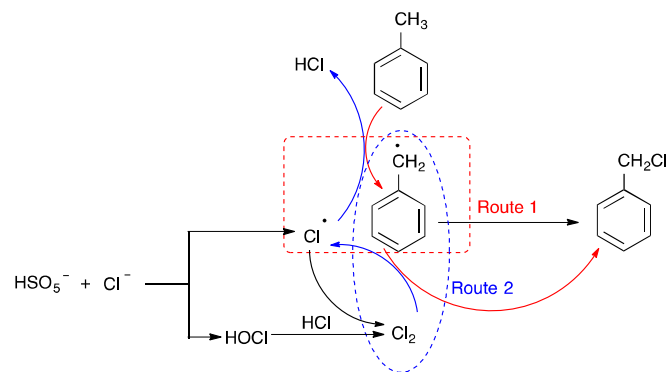
Other halogenation reactions

Our preliminary studies show that bromination of toluene with the $KHSO_5$/KBr system proceeds faster than its chlorination reaction. Under similar conditions to those of the chlorination of toluene, an 80% toluene conversion and a 56% benzyl bromide yield in 5 minutes, and a 100% conversion and a 75% yield in 15 minutes, were obtained. The fluorination and iodination attempts of toluene failed under similar halogenation conditions. In addition, our $KHSO_5$/KCl system was also able to chlorinate p-methylstyrene and ethylbenzene. A detailed investigation of these halogenation reactions and chlorination of poly(p-methylstyrene), polymer of p-methylstyrene is currently underway. Successful chlorination of poly(p-methylstyrene) to poly(p-chloromethylstyrene) will be a significant step in the easy preparation of quaternary ammonium ion based anion exchange resins.

Conclusions

We have demonstrated high α- and aromatic regioselective chlorination of toluene with the $KHSO_5$/KCl system at room temperature under catalyst-free conditions. The regioselectivity of the chlorine atom was strongly affected by the type of organic solvent in the solvent mixture. The chlorine containing solvents CH_2Cl_2, $CHCl_3$ and CCl_4 favoured the α-chlorination of toluene leading benzyl chloride as the major product via a radical mechanism, whereas the polar, water-miscible solvents C_2H_5OH, CH_3OH, and CH_3CN favoured the aromatic chlorination leading o-chlorotoluene and p-chlorotoluene as the major products via an electrophilic substitution mechanism. Compared to lab-scale and industrial methods for α- and aromatic chlorination reactions of toluene, our method is facile, efficient, and environmentally friendly. It appears to be applicable for the regioselective bromination of toluene and similar halogenation of other alkyl aromatics. Furthermore, the method utilizes many aspects important for green chemistry.

Experimental

Materials and Instrumentation

Toluene (Carlo Erba), Oxone, (Aldrich), potassium chloride (Riedel-de-Haen), and dichloromethane (Riedel-de-Haen) were used as received. The other reagents used were of research grade. The GC analyses of the oxidation of toluene reaction mixtures were performed using a Thermo Trace GC Ultra Gas Chromatograph fitted with an SE-54 Permabond fused silica capillary column (25 m, 0.32 mm i.d. and 0.25 mm film thickness) and an FID detector. The MS spectra were obtained with a GC-MS/MS (Thermo Finnigan PolarisQ) equipped with Wiley and NIST MS libraries.

General chlorination procedure

In a typical reaction, first 2.50 mL of organic solvent and 1.50 mL of water were mixed. Then 1.0 mmol toluene, 7.5 mmol KCl and 2.5 mmol Oxone (contains 5.0 mmol $KHSO_5$) were added sequentially to the mixture and the mixture content was stirred for 1 hour at room temperature. The organics in the mixture were extracted with dichloromethane and analyzed using the GC and GC-MS/MS instruments. The identification of the products was based on comparisons of their mass spectra to those in the library of the GC-MS/MS, and of the GC chromatograms of the sample solutions to those of the spiking experiments. (Examples of the GC chromatograms and a video material were supplied as Supporting Information).

Notes and references

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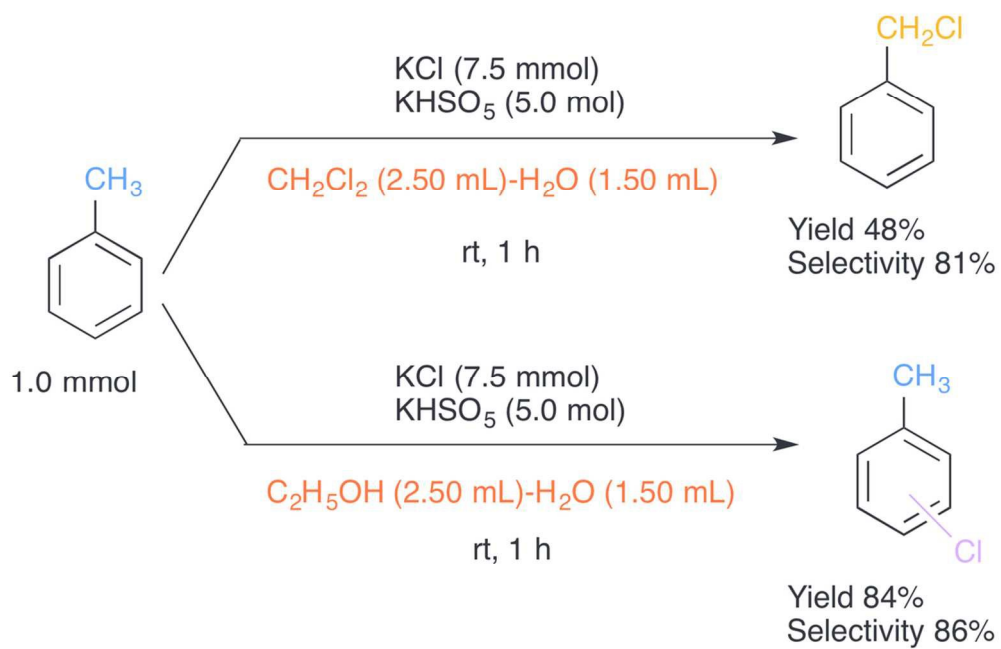
† The authors declare no competing financial interest.

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