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RESEARCH ARTICLE

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Sulfonyl chlorination of sulfonate-containing naphthol azo compounds

Abstract Chlorosulfonyl-containing naphthol azo compounds were prepared by reaction of the corresponding sulfonate-containing naphthol azo dyes with thionyl chloride in the presence of a catalytic quantity of *N*,*N*-dimethylformamide and various solvents. The yields and reaction selectivity of chlorosulfonyl-containing naphthol azo compounds were discussed according to the properties of solvents. It was demonstrated that high chemical selectivity and high yield were achieved by using benzene, toluene or thionyl chloride as solvent. Additionally, on account of unstable properties of sulfonyl chloride compounds in MS and ^{1}H-NMR analyses, a new analytical method using stable sulfonamide is put forward to verify the chemical structures of the corresponding sulfonyl chloride compounds indirectly.

Keywords azo compound, sulfonyl chlorination reaction, sulphonamide, structural identification

Sulfonyl chlorides are one kind of important intermediates in organic synthesis and widely used in preparation of sulfonamide and sulfonate ester compounds. Some sulfonyl chloride compounds bearing azo chromophore could also be used as precursors in instant photography [1]. As to arylsulfonate compounds without active groups, it is easily converted to their corresponding sulfonyl chlorides by using common sulfonyl chlorination reagents such as chlorosulfonic acid ($ClSO_3H$), thionyl chloride ($SOCl_2$), phosphorous pentachloride (PCl_5) and phosphorus oxychloride ($POCl_3$). As to complex arylsulfonate compounds bearing active groups, phosphorus oxychloride and thionyl chloride are always used as sulfonyl chlorination reagents, in which phosphorus oxychloride shows high chlorination selectivity while thionyl chloride has properties of reacting smoothly and handling easily. Fujita pointed out that phosphoryl chloride-*N*,*N*-dimethylacetamide ($POCl_3$-DMA) is a highly selective sulfonyl chlorination system for azo-compound bearing active groups but using thionyl chloride-*N*,*N*-dimethylformamide ($SOCl_2$-DMF) as sulfonyl chlorination system resulted in many by-products.

In the authors' previous research [2], for the conversion of some pyrazolone azo acid dyes into the corresponding sulfonyl chloride compounds, it was found that the reactions could be smoothly carried out in high yields (above 95%) without affecting any other functional groups by using the $SOCl_2$-DMF sulfonyl chlorination system. The high chlorination selectivity for the sulfonate group can be attributed to the stable hydrazone structure [3] of pyrazolone azo compounds. Jolanta [4] used $POCl_3$-DMA for sulfonyl chlorination of sulfonate-containing naphthol azo compounds (e.g. C.I. acid orange 7), in which acetonitrile and sulfolane were used as solvents but a large amount of DMA was needed and sulfolane could not be recycled easily due to its high boiling point. The approach proved difficult to scale up.

Up to now, there is no low-cost, highly effective and environment-friendly sulfonyl chlorination method for sulfonate-containing naphthol azo compounds. In this paper, three sorts of sulfonate-containing naphthol azo dyes C.I. acid orange 7 (**1a**), C.I. acid orange 12 (**1b**) and C.I. food yellow 3 (**1c**) (Fig. 1) were prepared by coupling reaction of diazo components (2-naphthol and 2-hydroxy-6-naphthalenesulfonate) and coupling components (aniline and sulfanilic acid). Then, the three dyes were sulfonyl chlorinated by use of the $SOCl_2$-DMF (solvent) sulfonyl chlorination system. The effects of $SOCl_2$, DMF and different solvents in the reaction were discussed and a new sulfonyl chlorination approach with high

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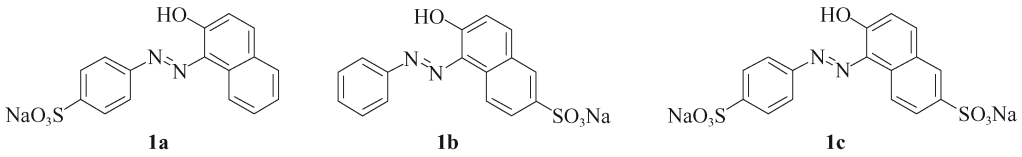

Fig. 1 Chemical structures of three sulfonate-containing naphthol azo dyes

yields, good selectivity and environmental compatibility is proposed.

In view of the instability of sulfonyl chloride compounds in structural analyses, their chemical structures were reverse-deduced from sulfonamide compounds derived from sulfonyl chlorides with simple alkyl amines.

1 Experimental

1.1 General methods

^{1}H-NMR spectra were recorded on a Varian INOVA 400 NMR Spectrometer with TMS as internal standard in $CDCl_3$. IR spectra were measured with an FT/IR-430 spectrophotometer. Mass spectra (MS) were determined by using a HP1100 mass spectrometer. Melting points were measured on a Mel-Temp capillary melting point apparatus and were uncorrected.

The synthesis of sulfonyl chloride compounds and their corresponding sulfonamide derivatives in different sulfonyl chlorination systems are shown in Fig. 2.

1.2 Synthesis of 4-[(2-chloro-1-naphthalenyl)azo]-benzenesulfonyl chloride (**4a**) : experiment No. 1

To a stirred suspended mixture of C.I. Acid Orange 7 (3.5 g, 0.01 mol) and thionyl chloride (20 mL), DMF (0.2 mL) was added at room temperature. The mixture was then heated to 60°C and stirred for 1.5 h. Then, the solvent and excess thionyl chloride were removed by vacuum distillation and the residue was transferred into ice water. After cooling to room temperature, the product was collected by suction filtration and washed with ice-cooled water till the filtrate was colorless and neutral, then dried in vacuum, yielding **4a** 3.3 g (94%). $t_m = 119°C–121°C$, $R_f = 0.85$ (developing reagent : toluene), $\lambda_m =$ 384 nm (in acetone). The reaction conditions and the results for the other sulfonyl chloride compounds are shown in Table 1.

1.3 Synthesis of *N*,*N*-diethyl-4-[(2-chloro-1-naphthalenyl) azo]-benzenesulfonamide (5a) : experiment No. 7

To a stirred suspension of sulfonyl chloride **4a** (1.7 g, 0.005 mol) in dry acetone (25 mL), K_2CO_3 (0.7 g, 0.005 mol) and diethylamine (0.7 mL, 25%, 0.01 mol)

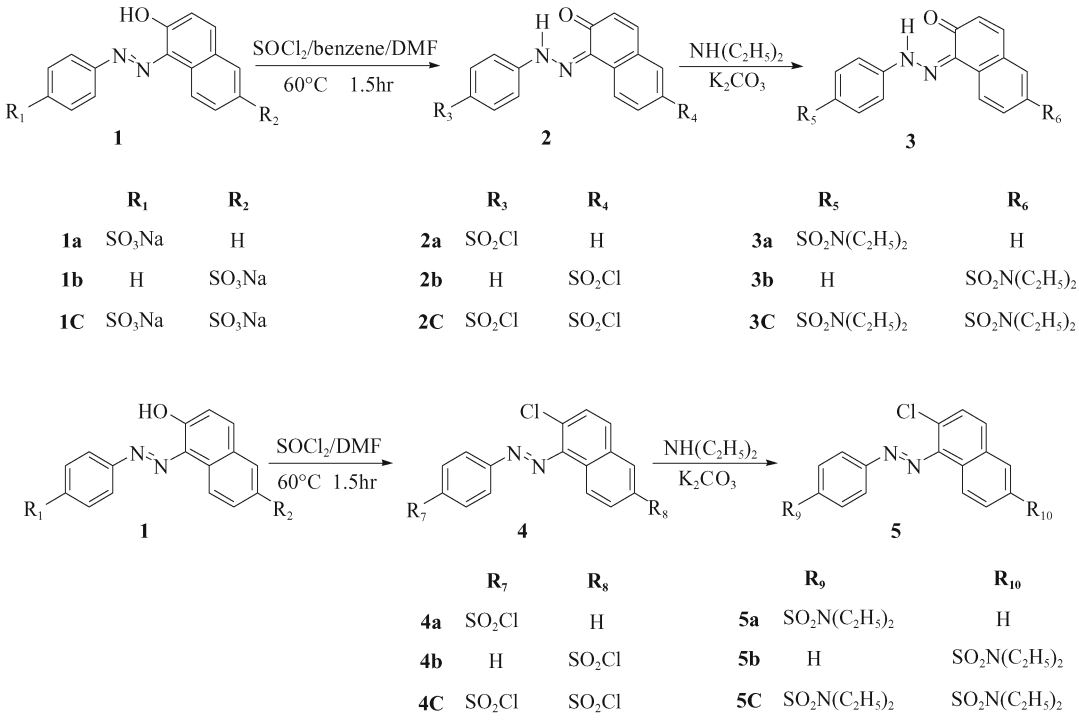

Fig. 2 Sulfonyl chlorination of sulfonate-containing naphthol azo compounds and amination of sulfonyl chlorides

Table 1 Reaction conditions and results of sulfonyl chlorination of sulfonate-containing naphthol azo compounds

experiment number	reactant	reaction conditions	product	yield and physical properties
2	**1a** (3.5 g)	same as experiment No.1 in addition to the solvent ($SOCl_2$, 20 mL) was replaced by benzene (20 mL) and $SOCl_2$ (2.2 mL)	**2a**	3.4g (97.1 %), $t_m = 206°C–208°C$, $R_f = 0.46$, $\lambda_m = 473$ nm
3	**1b** (3.5 g)	same as experiment No. 1	**4b**	3.5 g (99.2%), $t_m = 122°C–124°C$, $R_f = 0.83$, $\lambda_m = 455$ nm
4	**1b** (3.5 g)	same as experiment No. 2	**2b**	3.4 g (97.1%), $t_m = 212°C–214°C$, $R_f = 0.47$, $\lambda_m = 403$ nm and 472 nm
5	**1c** (2.3 g)	same as experiment No. 1 in addition to prolong reaction time to 7.5 h	**2c**	1.9 g (84.1%), $t_m = 228°C–230°C$, $R_f = 0.30$, $\lambda_m = 466$ nm
6	**1c** (2.3 g)	same as experiment No. 2 in addition to prolong reaction time to 3.5 h	**2c**	1.5 g (65.2%), $t_m = 228°C–230°C$, $R_f = 0.30$, $\lambda_m = 466$ nm

were added. The reaction mixture was stirred at room temperature for 1 h, then the solvent was entirely distilled and the residue was poured into dilute hydrochloric acid (100 mL, 10%). The product was collected by suction filtration and washed with water till the filtrate was colorless and neutral, then dried at ambient temperature, yielding **5a** 3.3 g (82.3%). $t_m = 172°C–174°C$, $R_f = 0.40$ (developing reagent : toluene), $\lambda_m = 365$ nm (in acetone). The reaction conditions and results of the other sulfonamide compounds are shown in Table 2.

In Table 1 and Table 2, R_f was measured in toluene and λ_m was measured in acetone.

1.4 Conductometric titration for determination of chloride content in sulfonyl chloride compounds

The sulfonyl chloride compound (0.100 g) was hydrolyzed in NaOH solution (0.1 mol/L, 40 mL) at boiling point for a period of time in order to completely convert chlorine in sulfonyl chlorides into chloride ions. After cooling to room temperature, the pH value of the solution was adjusted to about 2 with dilute nitric acid. Then, the chloride ion was titrated with a standard solution of silver nitrate. The endpoint was indicated by the conductometer. The chlorine content of sulfonyl chlorides could be calculated according to Eq. (1):

$$x = \frac{c\,M(v_1 - v_2)}{1000\,m} \quad (1)$$

where x is the chlorine content of sulfonyl chloride, c is the molar concentration of silver nitrate (mol/L), M is the molecular weight of sulfonyl chloride, v_1 is the original volume of silver nitrate (mL), v_2 is end volume of silver nitrate (mL) and m is the mass of sulfonyl chloride (g).

2 Results and discussion

In this research, thionyl chloride, one of the most commonly used chlorination reagents in industrial production, was selected as the chlorination reagent for C.I. Acid Orange 7 owing to the advantages of easy post-treatment, mild reaction conditions and recyclability. Subsequently, the effects of DMF and some other solvents in sulfonyl chlorination systems were investigated in order to prepare target sulfonyl chloride compounds.

2.1 Effect of DMF in sulfonyl chlorination reaction

As shown in Table 3, there was no sulfonyl chloride product obtained in $SOCl_2$ or $SOCl_2$-benzene sulfonyl chlorination system without DMF. In contrast, sulfonyl chloride products **4a** and **2a** were easily synthesized by use of $SOCl_2$-DMF and $SOCl_2$-DMF-benzene as sulfonyl chlorination system, respectively. The addition of a catalytic amount of DMF (1%) could result in sulfonyl chloride products with high yields (above 94%).

Reaction conditions of experiments 3′ and 4′ were same like experiments 3 and 4 in exception whether DMF was added.

Table 2 Synthetic conditions and results of sulfonamide-containing naphthol azo compounds from sulfonyl chlorides

experiment number	reactant	reaction conditions	product	yield and physical properties
8	**2a** (1.7 g)	same as experiment No. 7	**3a**	1.6 g (83.6%), $t_m = 191°C–193°C$, $R_f = 0.10$, $\lambda_m = 477$ nm
9	**4b** (1.7 g)	same as experiment No. 7	**5b**	1.5 g (79.8%), $t_m = 110°C–112°C$, $R_f = 0.41$, $\lambda_m = 458$ nm
10	**2b** (1.7 g)	same as experiment No. 7	**3b**	1.6 g (83.6%), $t_m = 150°C–152°C$, $R_f = 0.09$, $\lambda_m = 410$ nm and 473 nm
11	**2c** (2.2 g)	same as experiment No. 7 and reaction time was prolonged to 2 h	**3c**	2.0 g (77.2%), $t_m = 207°C–209°C$, $R_f = 0.02$, $\lambda_m = 475$ nm

Table 3 Influence of DMF amount on sulfonyl chlorination

experiment number	chlorination system	V (DMF) : V (Solvent)	product	yield/%
3′	$SOCl_2$	0	–	0
4′	$SOCl_2$-benzene	0	–	0
3	$SOCl_2$-DMF	0.01	**4a**	94
4	$SOCl_2$-DMF-benzene	0.01	**2a**	98

Some papers [5] had reported that DMF is an effective and common catalyst in the preparation of acyl chloride or sulfonyl chloride compounds with thionyl chloride. DMF can react with thionyl chloride and generate Vilsmeier-Hacck intermediate **6** [5]. Then, the carbonium ion of intermediate **6** attacks the highly electronegative oxygen atom of the sulfonate group and generates intermediate **7**. **The latter is transformed into** intermediate **8** after removal of DMF by an SN_i mechanism. Finally, the target sulfonyl chloride product **9** is obtained by removal of a hydrogen ion from intermediate **8** (Fig. 3).

It is clearly seen in this sulfonyl chlorination system that DMF not only acts as a catalyst in sulfonyl chlorination of reactant **1a** but shows other effects as well during the preparation of sulfonyl chlorides in certain inert solvents.

It can be concluded from Table 4 that DMF aids dissolution of the acid dye **1a** in sulfonyl chlorination systems through comparison of the solubility of the dye in benzene and toluene before and after adding DMF. Before adding DMF, the reactant **1a** is hard to dissolve in the nonpolar or weakly polar solvents (benzene and toluene) because of the big gap in their polarities resulting in poor yields of sulfonyl chloride products in heterogeneous chlorination systems. DMF not only dissolves **1a** but is, itself, soluble in arenes. This helps in the dissolution of some **1a** in the solvent. Thus, it can be concluded that addition of DMF favors the dissolution of sulfonate-containing naphthol azo compound **1a** in inert solvents and accelerates the chlorination reaction at the same time (Fig. 4).

2.2 Effect of solvent polarity in chlorination reaction

As seen in Table 3, both sulfonyl chloride products showed high yields and good selectivity in two different polar solvents (benzene and thionyl chloride) under the same conditions using DMF as the catalyst and thionyl chloride as the chlorination reagent but the products were largely different. In view of the influence of solvent polarity on the sulfonyl chlorination reaction, some solvents were selected for investigating the relationship between solvent properties and sulfonyl chlorination results. The results are shown in Table 5.

As seen in Table 5, the sulfonyl chloride products prepared in the sulfonyl chlorination systems using weakly polar solvents such as benzene, cyclohexane, toluene and chloroform exhibited varying yields and selectivity. When benzene or toluene was used as solvent, reactant **1a** was difficult to dissolve. The addition of DMF can make a little of **1a** dissolve in the solvent and this improves the chances of collision between reactant molecules and thionyl chloride molecules. When some product – the sulfonyl chloride – is formed, the undissolved reactant little by little dissolves in the sulfonyl chlorination system ensuring successive generation of the product (see Fig 4). As

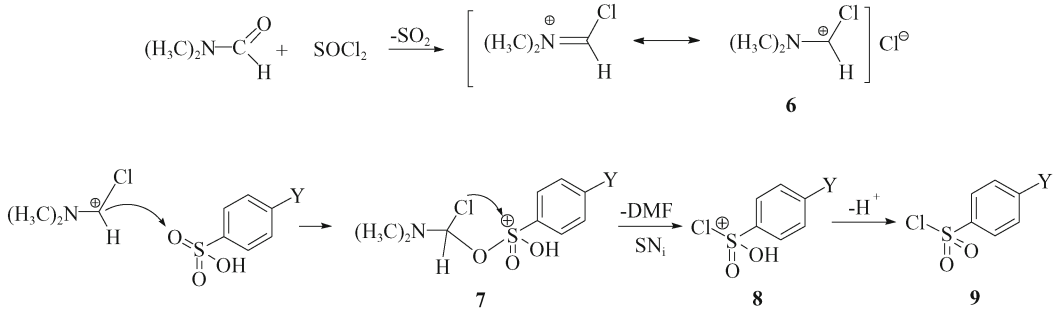

Fig. 3 Formation of Vilsmeier-Hacck intermediate and mechanism of sulfonyl chlorination

Table 4 Influence of DMF on the solubility of **1a** in different solvents

solvent	amount of DMF in 100 mL solvent/mL	solubility of **1a** in 100 mL solvent/mg
benzene	0	0
	1.0	15.5
toluene	0	0
	1.0	11.5

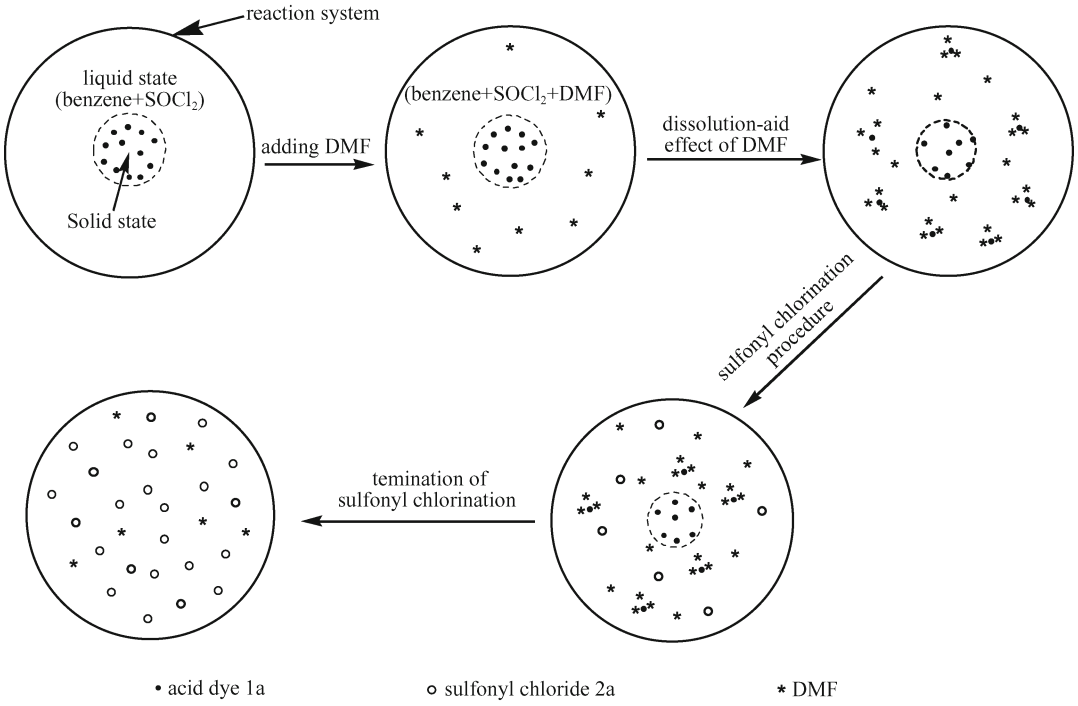

Fig. 4 Dissolution effect of DMF in the synthesis of sulfonyl chlorides

Table 5 Influence of physical properties of solvents on sulfonyl chlorination of sulfonate-containing naphthol azo compounds

solvent	b.p./°C	polarity/(10^{-30}C·m)	yield/%	product and purity	R_f (developing reagent : toluene)
benzene	80.1	0	98	**2a**, pure	0.46
cyclohexane	80.7	0	42	complex	–
toluene	110.6	1.23	89	**2a**, pure	0.46
chloroform	61	3.84	91	complex	–
thionyl chloride	76	5.27	94	**4a**, pure	0.85
tetrahydrofuran	66	5.70	–	–	–
ethyl acetate	77.1	6.27	–	–	–
acetonitrile	81.6	11.47	–	–	–

weakly polar solvents, benzene and toluene presented an obvious difference in yields. It could be seen in Table 4 that the solubility of **1a** in benzene (15.5 mg) was higher than that in toluene (11.5 mg), yielding 98% in benzene but 89% in toluene even as DMF was added in the same volume ratio. DMF is not soluble in cyclohexane. Thus, when cyclohexane was used as the solvent, the DMF dissolution effect vanished resulting in poor yield of the sulfonyl chloride product (42%). When chloroform was used as the solvent, the product was complicated (main product was **4a** and byproduct was **2a**). The result can be attributed to unstable chloroform decomposing into phosgene and hydrogen chloride in air even in the dark [6]. The decomposition of chloroform increased the chlorination capacity and partly chlorinated the hydroxy substituent of **1a**, which influenced the purity of sulfonyl chloride product.

When thionyl chloride was used as solvent and sulfonyl chlorination reagent simultaneously, its strong polarity did not favor the dissolution of the sulfonyl chloride product. However, excessive thionyl chloride could improve the chances of collision between reactant molecules and thionyl chloride molecules and result in high sulfonyl chlorination yields (94%). Excessive thionyl chloride increases the chlorination capacity of the sulfonyl chlorination reagent to reactive groups and decrease its chlorination selectivity to sulfonate group resulting in the complete formation of sulfonyl chloride product **4a** whose hydroxy group was chlorinated compared with sulfonyl chloride **2a**.

No sulfonyl chloride product was formed under the same sulfonyl chlorination conditions using strongly polar solvents such as acetonitrile, ethyl acetate and tetrahydrofuran. It could, therefore, be concluded that utilization of strongly polar solvent is not beneficial to the preparation of sulfonyl chloride from sulfonate-containing reactant.

Considering large-scale industrial production, the selected solvent in sulfonyl chlorination should be inert, low polarity, low toxicity, low cost, good solubility for

Table 6 Spectroscopic data of sulfonamide-containing naphthol azo compounds

compound	FT-IR/(KBr, cm^{-1})	^{1}H-NMR (400MHz, $CDCl_3$, Hz)	MS m/z/%
2a	1 623, 1 588, 1 372, 1 182	–	–
2b	1 614, 1 558, 1 374,1165	–	–
2c	1 622, 1 588, 1 571, 1 375, 1 171	–	–
3a	3 435, 2 978, 2 936, 1 619, 1 332, 1 159	16.20 (s, 1H), 8.45 (d, 1H, J = 8.4 Hz), 7.89 (d, 2H, J = 8.8 Hz), 7.69–7.73 (m, 3H), 7.54–7.58 (m, 2H), 7.40–7.45 (m, 1H), 6.75 (d, 1H, J = 9.6 Hz), 3.28 (q, 4H, 7.2 Hz), 1.16 (t, 6H, 7.2 Hz)	384 ([M+H]$^+$, 100)
3b	3 434, 2 970, 2 935, 1 617, 1 333, 1 150	16.25 (s, 1H), 8.71 (d, 1H, J = 8.8 Hz), 8.15 (s, 1H), 7.90 (d, 1H, J = 8.8 Hz), 7.79–7.83 (m, 3H), 7.50–7.55 (m, 2H), 7.38–7.41 (m, 1H), 7.05 (d, 1H, J = 9.6 Hz), 3.31 (q, 4H, 7.2 Hz), 1.16 (t, 6H, 7.2 Hz)	382 ([M-H]$^-$, 100), 440 ([M–H+Na+Cl]$^-$, 15)
3c	3 434, 2 976, 2 937, 1 619, 1 335, 1 150	16.25 (s, 1H), 8.60 (d, 1H, J = 8.4 Hz), 8.09 (s, 1H), 7.90–7.95 (m, 3H), 7.78–7.81 (m, 3H), 6.94 (d, 1H, J = 9.2 Hz), 3.30 (q, 8H, 7.2 Hz), 1.17 (t, 12H, 7.2 Hz)	519 ([M+H]$^+$, 100)
4a	1 616, 1 580, 1 378, 1 180, 717	–	–
4b	1 607, 1 578, 1 377, 1 165, 708	–	–
5a	2 977, 2 935, 1 618, 1 335, 1 160, 727	8.22 (m, 1H), 8.15 (d, 2H, J = 8.8 Hz), 8.04 (d, 2H, J = 8.8 Hz), 7.89 (m, 1H), 7.84 (d, 1H, J = 8.8 Hz), 7.60 (d, 1H, J = 8.8 Hz), 7.56–7.59 (m, 2H), 3.31 (q, 4H, 7.2 Hz), 1.20 (t, 6H, 7.2 Hz)	402 ([M+H]$^+$, 100), 404 ([M+2+H]$^+$, 43)
5b	2 972, 2 932, 1 613, 1 327, 1 156, 720	8.40 (s, 1H), 8.20 (d, 1H, J = 8.8 Hz), 8.04–8.08 (m, 2H), 7.89 (d, 1H, J = 9.2 Hz), 7.80–7.83 (m, 1H), 7.70 (d, 1H, J = 8.8 Hz), 7.60–7.62 (m, 3H), 3.30 (q, 4H, 7.2 Hz), 1.15 (t, 6H, 7.2 Hz)	424 ([M+Na]$^+$, 100), 426 ([M+Na+2]$^+$, 40), 402 ([M+H]$^+$, 21), 404 ([M+2+H]$^+$, 8)

catalyst DMF and a suitable boiling point. As seen in Table 5, the target sulfonyl chloride product bearing hydroxy group was synthesized by use of benzene or toluene as solvent. But benzene has high toxicity and mutagenicity and long-term exposure to it will cause impairment of workers' hematopoietic systems and even leukemia. Benzene should be avoided as much as possible in industry. Toluene is a commonly used chemical with less toxicity than benzene and no obvious damage to workers' hematopoietic system. Thus, toluene is recommended as solvent for sulfonyl chlorination systems in industrial production.

2.3 Characterization of sulfonyl chloride products

As a very reactive compound, sulfonyl chlorides are easy to hydrolyse, alcoholyse and ammonolysed during ^{1}H-NMR and mass spectrometry measurements. In order to help confirm the chemical structure of sulfonyl chloride, a simple amination reaction is used in laboratory. It is known that amination of sulfonyl chloride is convenient, quick, complete and does not change the main structure of the sulfonyl chloride compound. By integrative analyses of FT-IR, ^{1}H-NMR and mass spectrometry of sulfonamide derivatives (Table 6) as well as FT-IR (Table 6) and chlorine content analysis (Table 7) of the corresponding sulfonyl chlorides, the actual chemical structures of sulfonyl chloride can be easily deduced (Fig. 2).

Table 7 Chlorine content of sulfonyl chloride-containing naphthol azo compounds

sulfonyl chloride compound	chlorine content/%	
	calculated	theoretical
2a	10.2	10.2
2b	10.2	10.2
2c	15.9	16.0
4a	9.8	9.8
4b	9.8	9.8

The theoretical chlorine contents of **4a** and **4b** only include the content of chlorine in sulfonyl chloride group because chlorine atom connecting aryl couldn't hydrolyze in boiling NaOH solution.

There exists tautomerism between azo and hydrazone tautomers in naphthol azo compounds whose hydroxy group is at the ortho position of the azo group. It was reported [3] that most of 1-phenylazo-2-naphthol dyes are mixtures of hydrazone tautomer and azo tautomer. The hydrazone tautomer is the dominant form in the solid state. Among the methods of analyzing the main component of these naphthol azo dyes, the detection of a proton in the imino group is the most reliable and direct evidence for the existence of the hydrazone tautomer [7]. The intramolecular hydrogen bonding between the carbonyl group and the imine hydrogen makes the proton appear in ^{1}H-NMR spectrum at remarkably low field. As seen in Table 6, the proton in the imino group of sulfonamide

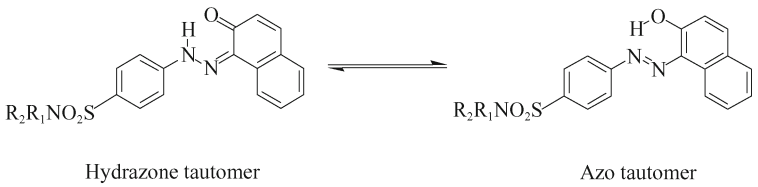

Fig. 5 Azo-hydrazone tautomerism of sulfonamides

appears at δ 16.20, δ 16.25 and the hydrogen integral is close to 1, which indicates that the sulfonamide-containing 1-phenylazo-2-naphthol compounds mostly exist in hydrazone form (Fig. 5).

In the experiment, bisulfonate-containing azo compound **1c** was converted to the same sulfonyl chloride product **2c** in either $SOCl_2$-DMF-benzene/toluene or $SOCl_2$-DMF sulfonyl chlorination system. However, monosulfonate-containing azo compounds **1a** and **1b** were converted to different sulfonyl chloride products **2a**, **4a** and **2b**, **4b** respectively in $SOCl_2$-DMF-benzene/toluene and $SOCl_2$-DMF sulfonyl chlorination systems. The results indicate that the existence of more electron-withdrawing group in sulfonate-containing azo compounds could effectively reduce electron density in conjugated systems and avoid chlorination of active hydroxy groups.

3 Conclusions

In this paper, a cost-effective sulfonyl chlorination system ($SOCl_2$-DMF-benzene/toluene) for preparing chlorosulfonyl-containing naphthol azo compound from sulfonate-containing naphthol azo compounds without affecting the active hydroxy group at the ortho position of azo group has been developed. In the sulfonyl chlorination system, DMF acts as catalyst and cosolvent simultaneously. Toluene is selected as the solvent due to its lower toxicity compared to benzene. The sulfonyl chlorination system offers several advantages including mild reaction conditions, high yields and high chlorination selectivity, which makes the sulfonyl chlorination procedure easy to scale up.

Moreover, the chemical structures of sulfonyl chloride compounds prepared from sulfonate-containing naphthol azo compounds **1a**, **1b** and **1c** were confirmed by analyses of FT-IR, chlorine content of sulfonyl chlorides and FT-IR, ^{1}H-NMR and mass spectrometry of their corresponding sulfonamide derivatives.

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