Preparation of Sodium Sulfonates Using by Copper as Catalyst

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The sodium alkyl sulfonates were prepared by Strecker reaction. The synthesis of sodium chloroethyl sulfonate from dichloroethane and sodium sulfite with different catalysts, it was found that copper was an efficient catalyst with a yield (81 %). The reaction conditions were also optimized to make the route more competitive and suitable for large-scale industrial production. Besides, some more sulfonates were also obtained with copper as catalyst *via* Strecker reaction.

Keywords: Sodium sulfonate, Chloro-hydrocarbons, Copper, Catalyst, Strecker reaction.

INTRODUCTION

Sulfonates and their derivatives play an important role in pharmaceutical, industrial and chemical manufacturing. For example, aliphatic and aromatic sulfonates are frequently utilized as anionic surfactants in detergents[1-5]. Substituted aromatic and aliphatic sulfonates are also widely used in the pharmaceuticals and dyes[6-9]. Moreover, in organic chemistry, some low-molecular weight sulfonic acids are often used as acid catalysts for esterification, alkylation and condensation reactions[10-12]. So, sulfonates have attracted considerable research interest. There are numbers of synthetic methods for sulfonates and a wide variety of applications of these methods were reviewed comprehensively in the literature[13-17]. Among the methods, perhaps the Strecker reaction[18] is one of extraordinary classical and convenient methods. Nevertheless, the normal raw material for Strecker reaction were bromo-hydrocarbons or iodo-hydrocarbons, which could lead to lower reactant atoms utilization, higher cost compared with chloro-hydrocarbons. Thus developing new methods with chloro-hydrocarbons as the raw material has good prospect from an industrial point of view.

2-Chloro-ethanesulfonic sodium is a functional intermediate for synthesizing the biological buffer and also used as pharmaceutical intermediate[19]. Recently, our group has focused on its synthesis from dichloroethane and sodium sulfite in the presence of different catalysts. It was found that 2-chloro-ethanesulfonic sodium can be generated in good yield with copper as the catalyst. Compared with the traditional method using bromo-hydrocarbons or iodo-hydrocarbons as raw material, the method reported in this paper has lower cost and offers

potential for large-scale industrial process. Furthermore, we also investigated the applicability of copper as the catalyst in the Strecker reaction and found that it performed well for short-chain chlorinated alkanes.

EXPERIMENTAL

Reagents and solvents were obtained from commercial suppliers. NMR spectra were recorded on Varian Inova-600 MHz NMR spectrometer with TMS as an internal reference. General procedure

Dichloroethane (27 mL, 343.6 mmol), anhydrous sodium sulfite (11 g, 84.5 mmol) and copper powder (50 mg) were added to a solution of 120 mL water and 110 mL ethanol in a three-necked flask equipped with a stirrer and a conderser. The reaction mixture was heated under refluxing for 22 h. Then it was cooled to room temperature. The retained dichloroethane was distilled off and the aqueous solution evaporated to dryness. The residue was then washed with hot ethanol and the combined ethanol phases then evaporated to dryness. In this manner, we obtained 2-chloro-ethanesulfonic sodium salt (81 %).

Sodium 2-phenoxyethansesulfonate: White solid, Yield: 82.3 % (lit[20] 43 %), Reaction time: 22 h. ^{1}H NMR (600 MHz, D$_2$O), δ (ppm): 7.00-7.35 (5H, m, ArH$_5$), 4.36-4.38 (2H, t, J = 6.0 Hz, CH$_2$), 3.32-3.34 (2H, t, J = 6.0 Hz, CH$_2$). ^{13}C NMR (150 MHz, D$_2$O) δ (ppm): 157.73, 129.92, 121.77, 115.08, 63.39, 50.23.

Sodium 2-chlorobenzylsulphonate: White solid, 92.1 %, 1 h (lit[21] 5 h) ^{1}H NMR (600 MHz, D$_2$O), δ(ppm): 7.31-7.46 (4H, m, ArH$_4$), 4.34 (1H, s, CH$_2$). ^{13}C NMR (150 MHz, D$_2$O),

δ(ppm): 134.39, 132.48, 129.74, 129.70, 129.55, 129.20, 53.84.

Sodium methyl 2-sulfoacetate: White solid, 83.4 %, 2 h. ^{1}H NMR (600 MHz, D_2O), δ (ppm): 3.97 (2H, s, CH_2), 3.77 (3H, s, CH_3). ^{13}C NMR (150 MHz, D_2O), δ(ppm): 167.52, 55.78, 52.26.

Sodium 2-hydroxyethanesulfonate: White solid, 77.4 %, 22 h. ^{1}H NMR (600 MHz, D_2O), δ(ppm): 3.89 (2H, s, CH_2), 3.30 (OH, s), 3.10 (2H, s, CH_2).^{13}C NMR (150 MHz, D_2O), δ(ppm): 56.99, 52.86.

Sodium 1-butanesulfonate: White solid, 65.2 %, 40 h. ^{1}H NMR (600 MHz, D_2O), δ(p pm): 2.88 (2H, d, CH_2), 1.68 (2H, t, CH_2), 1.40 (2H, t, CH_2), 0.90 (3H, d, CH_3). ^{13}CNMR (150 MHz, D_2O), δ(ppm): 50.87, 26.17, 21.16, 12.97.

Sodium 1-pentanesulfonate: White solid, 61.4 %, 40 h (lit[23]). ^{1}H NMR (600 MHz, D_2O), δ(ppm): 2.86 (2H, s, CH_2), 1.69 (2H, s, CH_2), 1.301.36 (4H, d, CH_2, CH_2), 0.85 (3H, s, CH_3). ^{13}C NMR (150 MHz, D_2O), δ(ppm): 51.10, 29.97, 23.70, 21.57, 13.15.

Sodium cyclopentanesulfonate: White solid, 49.2 %, 40 h. ^{1}H NMR (600 MHz, D_2O), δ(ppm): 3.32 (1H, s, CH), 1.58-1.96 (8H, m). ^{13}C NMR (150 MHz, D_2O), δ(ppm): 59.77, 28.3725.70.

Sodium dodecanesulphonate: White solid, 48.7 % (lit[24] 70 %), 40 h. ^{1}H NMR (600 MHz, DMSO), δ(ppm): 0.86 (3H, s, CH_3), 1.24 (18H, s) 1.55 (2H, s). ^{13}C NMR (150 MHz, D_2O), δ(ppm): 51.47, 31.26, 29.03, 28.93, 28.88, 28.68, 28.39, 25.03, 22.06, 13.92.

Sodium 2-chloro-ethanesulfonate: White solid, 81 %. ^{1}H NMR (600 MHz, DMSO), δ(ppm): 3.82-3.84 (2H, t, J = 6Hz,CH_2), 3.31-3.33 (2H, t, J = 6 Hz, CH_2). ^{13}C NMR (150 MHz, D_2O), δ(ppm): 52.89, 39.98.

RESULTS AND DISCUSSION

The reaction of dichloroethane and sodium sulfite is a two-phase reaction,which inhabits efficient mixing of reaction mixture. With considering of 1,4-dioxane possessing good miscibility with water and organic solvents, it was employed as the solvent for this. Unfortunately, but only low yield (35.8 %) of sodium chloroethyl sulfonate was obtained. Even in the presence of tetrabutyl ammonium bromide, the yield of target compound (40.6 %) was still unsatisfied. Furthermore, potassium bromide or sodium iodide was used as the catalyst. Nevertheless, they did not lead to excellent result (30.3 % for potassium bromide, 34.2 % for sodium iodide). According to the reported literature[20], we employed copper as the catalyst and found that it could accelerate the reaction much better than the catalysts above and had a good yield (58.7 %). Besides, cuprous chloride was also employed in our reaction, however, the result (47.1 %) was no better than copper. It was found that copper was a catalyst with good performance for the reaction. In view of the immiscibility of the water and organic phase, the mixture of water and alcohol was employed as the solvent instead of water only and it was found that the yield was further improved (62.4 %). The results are summarized in Table-1.

If the reaction parameters was inappropriate, the reaction might produce disubstituted by-product. Based on the research above, the reaction time and molar ratio were optimized to

TABLE-1 SELECTING OF CATALYST[a]		
Entry	Catalyst	Yield (%)
1	TBAB	40.6
2	KBr	30.2
3	NaI	34.2
4	CuCl	47.1
5	Cu	58.7
6	Cu[b]	62.4

[a]dichloroethane: sodium sulfite:2.5:1 (mol) reaction time:12 h solvent: water, [b] solvent: the mixture of water and alcohol

make the route more competitive from an industrial point of view with copper as the catalyst. The results are summarized in Tables 2 and 3. It was revealed that at first the yield increased as the reaction time prolonged. However, when the reaction time was over 22 h, the yield increased slightly with the further prolongation of reaction time. The yield decreased with the reaction time prolonging to 24 h. 2-Chloro-ethanesulfonic sodium is water-soluble and is easier to react with sodium sulfite than dichloroethane. As a result, long reaction time probably lead to the generation of disubstituted by-product and the decrease of yield. Therefore the reaction time should not exceed 22 h. It was also found that the effect of molar ratio on the yield was similar to reaction time to some extent. The increase of molar ratio promoted the improvement of the yield initially. Yet when it was over 4, it did not do much great help to the yield. Under the optimized reaction parameters as above, the yield of the reaction increased to 80.4 % making it more suitable for large-scale industrial production.

TABLE-2 EFFECT OF REACTION TIME ON THE REACTION[a]		
Entry	Time (h)	Yield (%)
1	16	68.5
2	18	72.4
3	20	79.2
4	22	80.4
5	24	68.8

[a] dichloroethane: sodium sulfite:5:1(molar ratio)

TABLE-3 EFFECT OF MOLAR RATE ON THE REACTION[a]		
Entry	Molar ratio	Yield (%)
1	2:1	63.5
2	3:1	74.4
3	4:1	81.0
4	5:1	80.4

[a] molar ratio: dichloroethane: sodium sulfite. reaction time: 22 h

Based on the good performance of copper as the catalyst in the reaction, more chloro-hydrocarbons as raw material were studied further. It was found that Cu has a catalytic activity for short-chain chlorinated alkanes. Compared with the reaction without copper as the catalyst, the yield of product **2a** and **2b** was improved dramatic--ally[21] and the reaction time of product **2c** and **2d** was shortened[22]. In addition, our reaction conditions could also tolerate other functional groups such as hydroxy, carbonyl, alkoxy and so on. However, with the increasing of carbon atoms of the reactants (**2e-f**), the yield was not satisfactory. It was shown evidently by secondary chloro-hydrocarbons or high molecular weight chloro-hydrocarbons (**2g-h**). The steric hindrance and the limit of long carbon chain on the active site may be main reason that attributed to poor reactivity of the reactants, thus leading to the low yield. Yet

the yield could be improved through extending the reaction time. The results are summarized in Table-4.

TABLE-4
REACTIONS OF CHLORO-HYDROCARBONS WITH Cu

Entry	Product	Yield (%)	Reaction time (h)
2a		82.3	22
2b		77.4	22
2c		92.1	1
2d		83.4	2
2e		65.2	40
2f		61.4	40
2e		49.2	40
2f		48.7	50

Conclusion

In summary, the target product sodium 2-chloro-ethane-sulfonate was synthesized by a low-cost and practical process with Cu as the catalyst. The present synthetic method was also improved and optimized to be more effective, competitive and suitable for large-scale industrial production. In addition, some more aliphatic sulfonates were also obtained in good yield with copper as the catalyst.

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