



Synthesis and Characterization of Azo Aromatic Diacyl Chlorides

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A convenient and rapid method for the synthesis of azo aromatic diacyl chlorides has been developed. Eight azo aromatic diacyl chlorides have been synthesized from aromatic nitro acids by using xylene as solvent. Most reaction periods are less than 2 h and the products are obtained in excellent yields with high purity.

Key Words: Azo aromatic diacyl chloride, Nitro aromatic acid, Thionyl chloride, Dimethyl benzene.

INTRODUCTION

Aromatic azo compounds have played many important roles in chemistry and have attracted interest in organic synthesis. They are widely utilized as organic dyes^{1,2}, analytical reagents³ and radical reaction initiators⁴. In addition, they are also important units in the area of nonlinear optics⁵, optical storage media^{6,7}, photochemical switches⁸ and electronic devices⁹.

On the other hand, azo compounds have more recently found advanced potential applications in the field of communication and biomedicine^{10,11}. Azo polymers possess some special characters in photophysics and photochemistry such as photoorientation of azobenzene-functionalized liquid crystalline hyperbranched polymer¹², optical limiting property¹³, polarization hologram and surface relief gratings¹⁴, photochromism property, command surface, photoinduced birefringence and dichroism¹⁵. Not surprisingly, azo polymers of this kind are increasingly viewed as attractive candidate for a variety of materials applications. To develop new high performance materials endowed with stimuli-responsive properties, it is necessary to synthesize reactive aromatic azo diacyl chlorides.

Direct synthesis of azo derivatives can be accomplished by the reduction of nitroaromatics with metal hydrides¹⁶⁻¹⁸, zinc in strongly alkaline medium¹⁹ or dicobalt octacarbonyl²⁰. Many other methods for the preparation of azo compounds have been described in the literature²¹⁻²³. But these techniques have not been used to synthesize aromatic azo diacyl chlorides. Xiong *et al.*²⁴ described the synthesis of aromatic azo diacyl chlorides using glucose as the reductant of aromatic nitro acids and thionyl chloride as acylating agent. We have examined the synthesis of aromatic azo diacyl chlorides from

aromatic nitro acids. In our previous work, hexadecyl trimethyl ammonium bromide has been used as phase transfer catalyst for the first time²⁵. PCl_5 has also been used as effective acylating agent²⁶. However, all these methods have a limitation that the reaction time is much longer.

In continuation with our studies on the synthesis of aromatic azo diacyl chlorides, we decided to develop a new method to optimize reaction conditions. In the course of our studies on the acylation reaction, it was observed that the use of solvent can efficiently convert aromatic azo diacids to corresponding aromatic azo diacyl chlorides. Indeed, aromatic azo diacids were acylated to aromatic azo diacyl chlorides rapidly by using xylene as solvent. Eight aromatic azo diacyl chlorides with different ring substituents have been prepared in the presence of xylene (**Scheme-I**). All the reactions can be carried out smoothly and completed within 2 h in excellent yields. The structures of aromatic azo diacyl chlorides were confirmed by IR, ¹H NMR and elemental analysis.

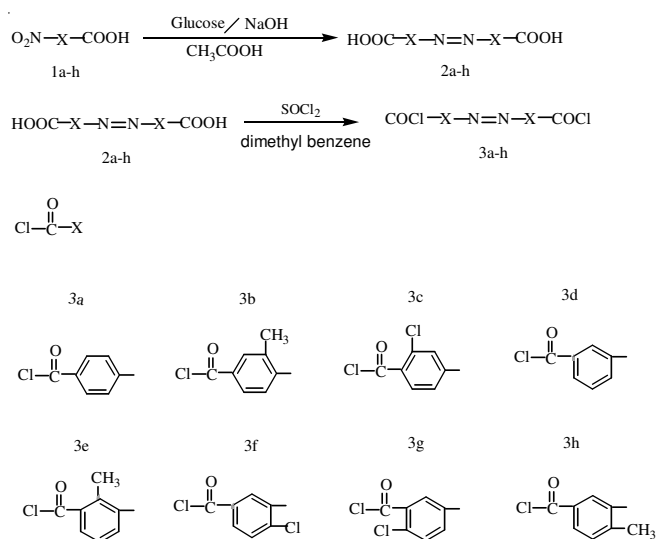
EXPERIMENTAL

Alfa Aesar China (Tianjin) Co. Ltd. supplied the following reagents: aromatic nitro acid, sodium hydroxide, glucose, glacial acetic acid, potassium carbonate, thionyl chloride, xylene, triethylamine, *n*-heptane. All reagents were of analytical grade and were used in their as-received state. Azo aromatic diacids were synthesized without further purification. During the experiments, distilled de-ionized water was used.

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a FTS-400 spectrophotometer in KBr. ¹H NMR spectra were measured on a Bruker DPX-400 M spectrometer using TMS as internal standard and CDCl_3 as solvent. Elemen-

tal analyses were performed on a PE-2400 CHN elemental analyzer.

General procedure for the preparation of aromatic azo diacyl chloride (3a-h): Aromatic nitro acid (40 mmol) **1a-h**, NaOH (25g, 616 mmol) and water (120 mL) were placed in a round bottom flask. Glucose (50 g, 228 mmol) in water (80 mL) was added over 0.5 h while stirring at 50-60 °C. The reaction mixture was stirred vigorously in air for 8 h ultimately affording a dark brown mixture. On cooling to room temperature, the mixture was acidified with glacial acetic acid to pH 6, filtered, washed with water and dissolved in hot potassium carbonate solution. The solution was acidified, filtered and washed with water again. Crude aromatic azo diacids **2a-h** were obtained and used in the next step without purification.



The crude aromatic azo diacid (14.5 mmol) **2a-h**, 30 mL thionyl chloride, 30 mL xylene and 0.3 mL triethylamine were placed in a 150 mL round bottomed flask. The mixture was refluxed for 2 h, until the suspension mixture was converted into a clear solution. Unreacted thionyl chloride was removed under reduced pressure. The residue was recrystallized from *n*-heptane and dried below 70 °C in a vacuum to yield the pure products. All the compounds gave satisfactory analytical and spectroscopic data.

Spectral data

Azobenzene-4,4'-dicarboxylic acid chloride (3a): m.p.: 164-165 °C; dark-red needles; yield 88 %; IR (KBr, ν_{\max} , cm^{-1}): 3095, 1778, 1734, 1596, 1577, 1475; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, 4H, $J = 7.2$ Hz, ArH), 8.32 (d, 4H, $J = 8.8$ Hz, ArH); For $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2\text{Cl}_2$: calcd: C, 54.72; H, 2.61; N, 9.12. Found: C, 54.96; H, 2.67; N, 9.48.

2,2'-Dimethylazobenzene-4,4'-dicarboxylic acid chloride (3b): m.p.: 181-183 °C; dark-brown needles; yield 92 %; IR (KBr, ν_{\max} , cm^{-1}): 3098, 2964, 2925, 1755, 1699, 1598, 1475, 1440; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ : 2.81 (s, 6H, CH_3), 7.65 (d, 2H, $J = 8.4$ Hz, ArH), 8.07 (d, 2H, $J = 8.8$ Hz, ArH), 8.14 (s, 2H, ArH); For $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2$: calcd: C, 57.3; H, 3.6; N, 8.4. Found: C, 57.4; H, 3.7; N, 8.5.

3,3'-Dichloroazobenzene-4,4'-dicarboxylic acid chloride (3c): m.p.: 153-154 °C; orange powder; yield 89 %;

IR (KBr, ν_{\max} , cm^{-1}): 3095, 1767, 1700, 1585, 1562, 1464; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.97 (d, 2H, $J = 8.0$ Hz, ArH), 8.06 (s, 2H, ArH), 8.28 (d, 2H, $J = 8.0$ Hz, ArH); For $\text{C}_{14}\text{H}_6\text{N}_2\text{O}_2\text{Cl}_4$: calcd: C, 44.7; H, 1.6; N, 7.45. Found: C, 44.9; H, 1.6; N, 7.6.

Azobenzene-3,3'-dicarboxylic acid chloride (3d): m.p.: 100-101 °C; bright-yellow needles; yield 93 %; IR (KBr, ν_{\max} , cm^{-1}): 3073, 1755, 1690, 1585, 1472; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.74 (t, 2H, $J = 8.0$ Hz, ArH), 8.28 (d, 4H, $J = 8.0$ Hz, ArH), 8.72 (s, 2H, ArH); For $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2\text{Cl}_2$: calcd: C, 54.72; H, 2.61; N, 9.12. Found: C, 55.09; H, 2.69, N, 9.54.

2,2'-Dimethylazobenzene-3,3'-dicarboxylic acid chloride (3e): m.p.: 184-186 °C; orange needles; yield 89 %; IR (KBr, ν_{\max} , cm^{-1}): 3095, 2972, 2937, 1755, 1691, 1569, 1440; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 2.96 (s, 6H, CH_3), 7.45 (t, 2H, $J = 8.4$ Hz, ArH); 7.87 (d, 2H, $J = 8.0$ Hz, ArH), 8.33 (d, 2H, $J = 8.0$ Hz, ArH); For $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2$: calcd: C, 57.3; H, 3.6; N, 8.4. Found: C, 57.6; H, 3.6; N, 8.5.

6,6'-Dichloroazobenzene-3,3'-dicarboxylic acid chloride (3f): m.p.: 219-221 °C; orange powder; yield 84 %; IR (KBr, ν_{\max} , cm^{-1}): 3086, 1759, 1691, 1564, 1695, 1465, 1444; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.79 (d, 2H, $J = 8.0$ Hz, ArH), 8.20 (d, 2H, $J = 8.0$ Hz, ArH), 8.46 (s, 2H, ArH); for $\text{C}_{14}\text{H}_6\text{N}_2\text{O}_2\text{Cl}_4$: calcd: C, 44.7; H, 1.6; N, 7.45. Found: C, 44.8; H, 1.6; N, 7.47.

4,4'-Chlorioazobenzene-3,3'-dicarboxylic acid chloride (3g): m.p.: 177-179 °C; orange powder; yield 81 %; IR (KBr, ν_{\max} , cm^{-1}): 3094, 1754, 1698, 1585, 1560, 1445; $^1\text{H NMR}$: δ 7.70 (d, 2H, ArH), 8.13 (d, 2H, $J = 8.0$ Hz, ArH), 8.69 (s, 2H, $J = 8.4$ Hz, ArH); for $\text{C}_{14}\text{H}_6\text{N}_2\text{O}_2\text{Cl}_4$: C, 44.7; H, 1.6; N, 7.45. Found: C, 44.9; H, 1.7; N, 7.6.

2,2'-Dimethylazobenzene-5,5'-dicarboxylic acid chloride (3h): m.p.: 170-172 °C; orange powder; yield 83 %; IR (KBr, ν_{\max} , cm^{-1}): 3089, 2957, 2851, 1747, 1695, 1595, 1571, 1448; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ : 2.86 (s, 6H, CH_3), 7.53 (d, 2H, $J = 8.4$ Hz, ArH), 8.15 (d, 2H, $J = 8.8$ Hz, ArH), 8.34 (s, 2H, ArH); for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2$: C, 57.3; H, 3.6; N, 8.4. Found : C, 57.8; H, 3.7; N, 8.5.

RESULTS AND DISCUSSION

In the acylation study, the crude azobenzene 4,4'-dicarboxylic acid and thionyl chloride were chosen as a model reaction in the presence of xylene. The optimum contents of xylene and reaction time were established by using the crude aromatic azo diacid (14.5 mmol), 30 mL thionyl chloride. The experimental results are summarized in Table-1. Without xylene, the acylating reaction time occurred 12 h and the yield was 75 %. If xylene was used for solvent, reaction temperature was raised to 110 °C, which implied that high temperature could promote the formation of azobenzene-4,4'-dicarboxylic acid chloride. It is considered that the presence of xylene may act as a media. Not only does it make the liquid and solid phase mixfully, but also it makes acylating reaction occur in mild condition and the reaction time was reduced significantly. The optimum contents of xylene (30 mL) is required for the complete acylating of azobenzene 4,4'-dicarboxylic acid within 2 h in 88 % yield. Owing to the ease of removal, the xylene could be recycled and reused.

TABLE-1
ACYLATION OF 4,4'-DICARBOXYLIC AZO ACID
IN THE PRESENCE OF XYLENE

Entry	Xylene (mL)	Reaction time (h)	Yield (%)
1	0	12	75
2	10	2	80
3	20	2	85
4	30	2	88
5	40	2	88
6	30	1	76
7	30	1.5	80
8	30	2	88
9	30	3	88
10	30	4	87

Conclusion

An efficient and rapid method is developed for the synthesis of aromatic azo diacyl chlorides by aromatic nitro acids with thionyl chloride in the presence of xylene. The significant advantages of it are: (a) operational simplicity (b) mild reaction conditions and excellent yields; (c) short reaction times. Therefore, this convenient and practical approach is anticipated to attract much attention.

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