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N,*N*′-Phosgenation with Triphosgene in the Synthesis of Direct Dyes containing the Ureylene Group

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ABSTRACT

Using triphosgene as a substitute for phosgene, many 'urea-containing' direct dyes or intermediates (i.e. containing the ureylene—NHCOHN—system) can be safely and conveniently synthesised. The phosgenation is affected by hydrolysis side-reactions and the yields of product are dependent on the relative reactivity of the reacting amino groups, pH, temperature and the excess of triphosgene used. J-acid urea, C.I. Direct Yellow 50, and C.I. Direct Red 75 were obtained in high yield (>93%) and with only a slight excess of triphosgene. Copyright © 1996 Elsevier Science Ltd

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INTRODUCTION

'Urea-containing' direct dyes, namely those containing the ureylene group, are widely used in the dyeing of wool, silk, cotton and other fabrics. Their traditional synthesis involves the condensation of phosgene with dyes containing an amino group, namely

$\text{Ar–N=N–Ar'–NO}_2 \rightarrow \text{Ar–N=N–Ar'–NH}_2$

$2\ \text{Ar–N=N–Ar'–NH}_2 + \text{COCl}_2 \rightarrow \text{Ar–N=N–Ar'–NH–CO–NH–Ar'–N=N–Ar} + 2\text{HCl}$

or from their 'urea-type' intermediate, e.g. J-acid urea, prepared using a similar method:

$2\ \text{Ar'NH}_2 + \text{COCl}_2 \rightarrow \text{Ar'NH–CO–NHAr'} + 2\ \text{HCl}$

Ar'NH–CO–NHAr $+2\ \mathrm{Ar{-}N_2}^{2+} \rightarrow$ Ar–N = N–Ar'–NH–CO–NH–Ar'–N = N–Ar.

Because phosgene is a gas and easy to diffuse, it has to be used in several fold excess, and, additionally, its toxicity often makes the syntheses potentially hazardous.

Triphosgene, or bis(trichloromethyl) carbonate (CCl_3–O–CO–$OCCl_3$) is a stable crystalline material (m.p. 79–80°C, b.p. 206°C) which is easy to transport, store and handle. It has recently been shown to be a useful and practical phosgene source in the phosgenation of amines, anilines, alcohols and phenols.[1–6] The phosgenation of direct dyes, however, needs to be in aqueous medium. We report here the initial research on the phosgenation with triphosgene in the preparation of direct dyes in aqueous solution.

EXPERIMENTAL

Triphosgene was prepared by the method similar to Eckert and Forster.[1] J-acid and other raw materials were commercial products from the Nanjin Chemical Plant. Analytical reagents are all analytically pure.

The general synthetic process is illustrated by the following: 2 g J-acid was added to 50 ml water, with dropwise addition of the 10% aq. NaOH to facilitate dissolution; the pH of the final solution was 6–8. The solution was then stirred, heated to 20–60°C and triphosgene powder rapidly added. The reaction was carried out at constant temperature 20–60°C and pH 6–8, and monitored by HPLC. When the reaction was complete, J-acid urea was obtained by salting-out. Results from different temperature, pH and triphosgene ratios are outlined in the following Results section.

HPLC was performed using an HP 1050 instrument made in U.S.A., LC column: ods 5 μ and pH meter measurements were made on a PHS-3C Precision pH Meter manufactured by the Shanghai Lei Ci Instrument Factory.

RESULTS AND DISCUSSION

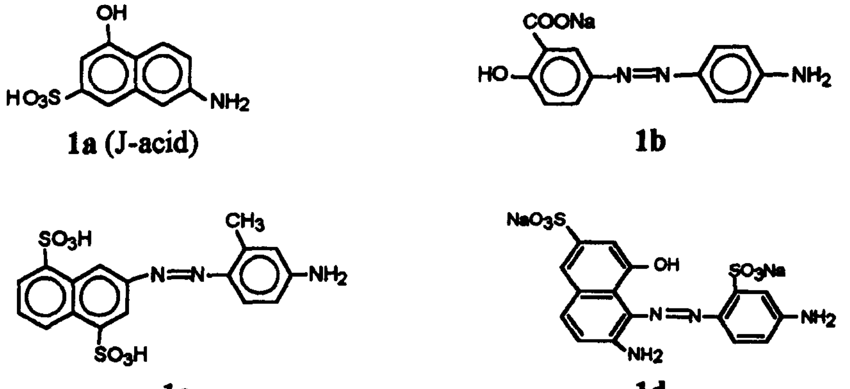
J-acid urea (**3a**), C.I. Direct Yellow 26 (**3b**), C.I. Direct Yellow 50 (**3c**) and C.I. Direct Red 75 (**3d**), all of the general formula: ArNH–CO–NHAr (**3**) were prepared by phosgenation with triphosgene (**2**) of the appropriate amines **1a–1d** (Scheme 1), respectively, using an essentially simple phosgenating process, namely: dissolving **1** in water, adjusing the pH of the solution with 10% aq. NaOH, adding triphosgene powder, and stirring it at a specific pH (controlled by the addition of 10% NaOH). The reaction pH, temperature and mole ratio of **1**:**2** added were the main factors influencing the reaction.

Effect of pH

Table 1 shows the influence of pH on the yields (η) of **3**. **3a** was obtained in higher yields in neutral and weakly alkaline media (pH: 7.0~8.0) than in a weakly acidic medium (pH: 6.0); **3b** was preferably obtained at pH 8.0 than at lower pH; a weakly acidic media (pH 6.0~6.5) was, however, more favorable for **3c**, and **3d** was obtained in highest yield in a neutral medium.

As suggested by Eckert and Forster,[1] the reaction mechanism for the release of phosghene from triphosgene is as shown in Scheme 2, where Nu is a nucleophilic catalyst such as triethylamine or pyridine, or is the reactant 1.

$$\underset{\mathbf{1}}{2\,\mathrm{Ar\text{-}NH_2}} + \underset{\mathbf{2}}{1/3\,\mathrm{CCl_3\text{-}O\text{-}CO\text{-}OCCl_3}} \longrightarrow \underset{\mathbf{3}}{\mathrm{ArNH\text{-}CO\text{-}NHAr}} + \mathrm{HCl}$$



1a (J-acid) **1b**

1c **1d**

Scheme 1

TABLE 1
Effect of pH

3	3a[a]			3b[b]			3c[c]				3d[d]		
pH	6.0	7.0	8.0	7.0	7.5	8.0	6.0	6.5	7.0	8.0	6.0	7.0	8.0
η (%)	85.4	94.6	95.0	5.2	9.1	30.8	78.4	77.8	69.5	35.8	84.4	95.4	83.5

[a] 40°C, 10 h, mole ratio of **1**:**2** = 1:0.34; [b] 20°C, 10 h, mole ratio of **1**:**2** = 1:0.17; [c] 20°C, 10 h, mole ratio of **1**:**2** = 1:0.17; [d] 40°C, 10 h, mole ratio of **1**:**2** = 1:0.25.

$Cl_3C\text{–}CO\text{–}OCl_3 + Nu \rightarrow Cl_3CO\text{–}CO\text{–}Nu^+ + Cl\text{–}CO\text{–}Cl + Cl^- \rightarrow 2\ Cl\text{–}CO\text{–}Cl + Cl\text{–}CO\text{–}Nu^+ + Cl^- \rightarrow 3\ Cl\text{–}CO\text{–}Cl + Nu$

$Cl\text{–}CO\text{–}Cl + Nu \rightarrow Cl\text{–}CO\text{–}Nu^+ + Cl^-$

$Cl\text{–}CO\text{–}Nu^+ + ArNH_2 \rightarrow Cl\text{–}CO\text{–}HNAr + H^+ + Nu$

$Cl\text{–}CO\text{–}HNAr + ArNH_2 \rightarrow ArNH\text{–}CO\text{–}HNAr + HCl$

A weakly alkaline medium is beneficial for the reaction of **1**, but hydrolysis also occurs to some extent under these conditions, namely

$Cl\text{–}CO\text{–}Nu^+ + OH^- \rightarrow HCl + CO_2 + Nu.$

The pH also affects the solubility of **1**. Thus, **1b** has poor solubility and reacts only slowly with **2** if pH < 8.0. Compound **1c**, however, is very soluble even at pH = 6.0, and better yields are obtained at pH 6.0 ~ 6.5 than at pH 7.0, since little hydrolysis occurs in a weakly acidic medium. For compounds **1a** and **1d**, pH 7.0 is the most suitable.

Effect of reaction temperature

With increasing temperature, the reaction rate accelerates accordingly. Table 2 shows the effect of temperature on the reaction of **1a**. At 20°C, it takes 15 h to complete the reaction, at 40°C it takes 10 h, while at 60°C it takes only 6 h. The yields of **3a** (J-acid urea) show little difference when the reaction is effected at different temperatures, but for **3b**, **3c** and **3d**, a higher temperature

TABLE 2
Effect of Temperature on Yields of **3a** (%)

T (°C)	2 h	4 h	6 h	8 h	10 h	12 h	15 h
20	—	—	—	63.1	68.4	—	89.3
30	—	—	—	79.2	89.3	91.0	—
40	69.1	—	88.6	90.4	93.1	—	—
50	75.2	—	91.0	93.5	—	—	—
60	81.8	85.1	90.0	—	—	—	—

pH = 7, mole ratio of **1**:**2** = 1:0.24.

TABLE 3
Effect of Temperature on Yields (%)

T (°C)	**3b**[a]	**3c**[b]	**3d**[c]
20	30.8	69.5	95
30	—	—	75
40	34.8	61.4	60
60	30.5	55.0	—

[a] pH 8.0, **1**:**2** (mol) 1:0.34, 10 h; [b] pH 7.0, **1**:**2** (mol) 1:0.17, 10 h; [c] pH 7.0, **1**:**2** (mol) 1:0.20, 10 h.

results in lower yields (Table 3). This is due to the hydrolysis of triphosgene at the higher temperature, especially at the higher pH (8.0) reaction medium used for **1b** (Table 3).

The use of a lower temperature (20°C) is beneficial for the synthesis of **3c** and **3d**, whilst a higher temperature (40 ~ 50°C) is more appropriate for the preparation of **3a**. This is the result of the competition between phosgenation and hydrolysis. At 20°C, and prolonging the reaction time to 24 h, **3c** may be obtained in high yield (95.6%), but the yield of **3b** never reaches such a value.

1:2 mole ratio

Stoichiometrically, the mole ratio of **1**:**2** should be 1:0.17, but because of the hydrolysis side reaction of **2** in the aqueous medium, more triphosgene is needed to complete the reaction.

From Table 4, it is apparent that the more **2** is used, the faster is the reaction of **1a**. Whilst the excess of **2** increases the reaction rate of **1a**, the yields of **3a** are not increased very much and, therefore, for **3a** the optimum molar ratio of **1**:**2** is 1:0.25 ~ 0.34.

The excess of **2** has little influence on the yields of **3d** (Table 5), which implies that **2** has good selectivity to **1d**. However, **3b** and **3c** need the excess, especially when the reaction is carried out in the alkaline medium (pH 8.0) used for **3b** (Table 5).

TABLE 4
Effect of **1**:**2** Ratio on Yields (%) of **3a**

1:2 (mol)	2 h	6 h	8 h	10 h
1:0.17	51.7	80.1	84.2	87.2
1:0.25	75.2	85.0	89.1	93.4
1:0.34	80.3	92.4	94.3	95.3
1:0.40	92.0	96.4	—	—

pH = 7, T = 50°C.

TABLE 5
Effect of **1**:**2** Ratio on Yields of **3**

1:2 (mol)	**3b**[a]	**3c**[b]	**3d**[c]
1:0.17	20.7	69.5	94.0
1:0.20	—	—	95.5
1:0.34	34.8	78.9	96.0
1:0.51	48.6	87.6	—

[a] pH 8.0, T 40°C, 10 h. [b] pH 7.0, T 20°C, 10 h. [c] pH 7.0, T 20°C, 10 h.

CONCLUSION

With triphosgene, the phosgenation of soluble amino-containing dyes and intermediates can be carried out, with safety and simplicity to form 'urea-containing' direct dyes or intermediates. The reaction is accompanied by hydrolysis of the triphosgene. The yields are affected by the reactivity of the amino groups, pH, temperature and the excess of triphosgene used. The method could be applied to the large-scale manufacture of J-acid urea, C.I. Direct Yellow 50, C.I. Direct Red 75 and related direct dyes and intermediates.

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