Available online at www.sciencedirect.com
SCIENCE DIRECT®
Dyes and Pigments 60 (2004) 85–90
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Novel fibre-reactive triazinyl betaines: a one step synthesis of 4-*m*-carboxypyridinium-*s*-triazine-2-oxides from dichloro-*s*-triazinyl derivatives

A.H.M. Renfrew*, I. Bates, V. Kampyli, D.A.S. Phillips

Chistian Doppler Laboratory for Cellulosic Fibre and Textile Chemistry, UMIST, PO Box 88, Manchester M60 1QD, UK

Received 9 May 2003; received in revised form 1 June 2003; accepted 12 June 2003

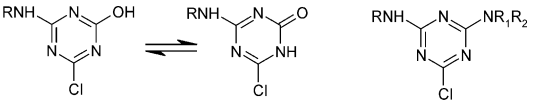
Abstract

Five dichlorotriazinyl compounds have been reacted in turn, with nicotinic acid and one with pyridine, in acid medium. In each case either a carboxypyridinium or a pyridinium-triazine-2-oxide was formed cleanly. Ring opening of the pyridinium ring attached to the triazine did not occur. A limited study suggests that a bis-pyridinium-triazine is the penultimate species and chlorohydroxytriazines [6-chloro-1,3,5-triazin-2(1H)-ones] are not intermediates in the reaction sequence.

Keywords: Dichlorotriazine; Triazine-2-oxide; Nicotinic acid; Heterocyclic betaine; Zinke; Fujiwara

1. Introduction

4-(Substituted)-amino-6-chloro-1,3,5-triazin-2(1H)-one (CTO) compounds **I**, unlike the corresponding aminochloro-*s*-triazinyl derivatives (**II**; R_1,R_2 = H, alkyl or aryl), do not react significantly with cellulosic fibres in an alkaline medium. However, the chlorine atom is susceptible to acid catalysed nucleophilic displacement and a recent paper [1] describes the transformation of the CTO group, in acid medium, into novel pyridinium-s-triazine-2-oxide derivatives (III; R = *p*-sulphophenyl; R_1 = H or CO_2H) which are fibre reactive in alkaline medium (Scheme 1).



I II

CTO compounds are generally prepared by alkaline hydrolysis of dichloro-*s*-triazinyl (DCT) precursors (Scheme 2).

The reaction of DCT compounds with pyridine and substituted pyridines, in acid medium, has not been reported. However, there are countless examples in the literature [2] of the reaction of (substituted) pyridines with monochloro-s-triazinyl (MCT) derivatives and this reaction is generally carried out at pH < 7. For DCT compounds several reaction pathways are possible, and all offer the prospect of leading to triazine-2-oxide derivatives (**III**; Scheme 3).

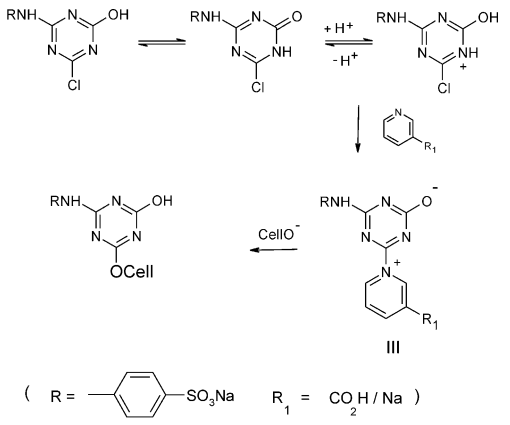
* Corresponding author.

0143-7208/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0143-7208(03)00126-8

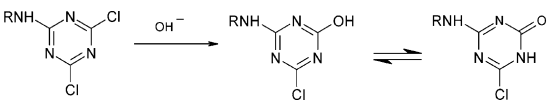
It is known that strongly activated halogen atoms attached to both aromatic and heteroaromatic rings (including DCT compounds), on treatment with pyridine and caustic soda solution undergo the Zinke [3,4] and the closely related Fujiwara [5] reactions. The former involves stepwise and the latter, simultaneous, addition of the two reagents and both Name Reactions form the basis of colorimetric analytical methods [6] for determining the concentrations of such compounds. For DCT compounds, the precise mechanistic details of the Zinke and the Fujiwara reactions are unclear, but both reactions are believed [6] to involve initial quaternisation, followed by base catalysed ring opening of the so formed pyridinium rings and subsequent formation of a triazinyl substituted monoanil of glutaconic dialdehyde (**V**; Scheme 4). This is the origin of the intense yellow coloration.

It has also been reported that cyanuric chloride reacts with pyridine [7,8] in the absence of alkali, to give, unexpectedly, triazine derivatives **VI** and **VII** which contain an α- and/or γ-(substituted) pyridyl group, depending on conditions. However, this reaction has also been studied by Tsujikawa [9] who subsequently showed the reaction product to be the heterocyclic betaine (**VIII**).

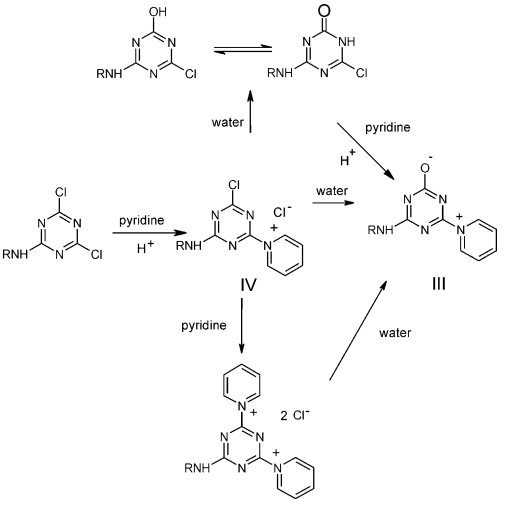
Accordingly, monochloro-*s*-triazines and cyanuric chloride react with pyridine, in acid medium, to furnish pyridinium derivatives and ring opening of the pyridinium ring does not occur. In the case of DCT compounds, the first step of the Zinke and Fujiwara reactions is formation of a pyridinium salt, with ring opening subsequently being induced by attack with hydroxide ion. The products of this reaction, in the absence of alkali, have not been investigated.



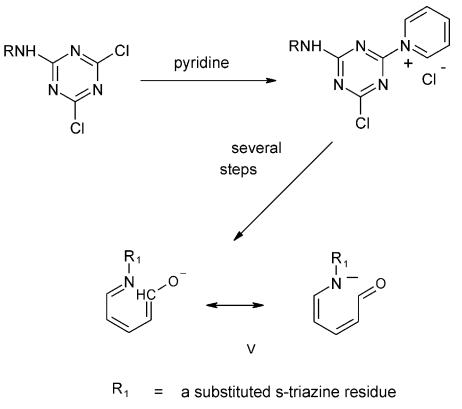
Scheme 1.



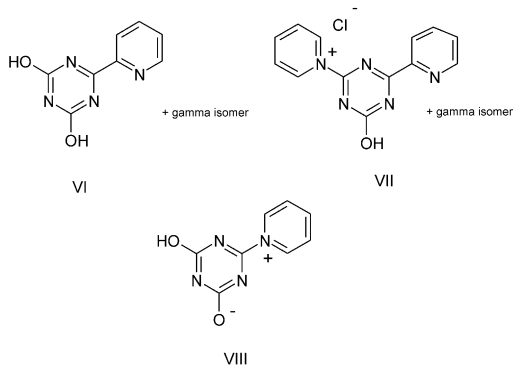
Scheme 2.



Scheme 3.



Scheme 4.



This paper describes the reaction of five DCT compounds with nicotinic acid, and, in one case, with pyridine, in acid medium. Progress of each reaction was monitored by HPLC and the resulting products evaluated.

2. Experimental

HPLC was performed with a Hewlett Packard 1100 series fitted with a quaternary pump. The column was a 10 cm Purospher RP-18 (5 μm) packing and a LiChocart 125-4 HPLC column cartridge; solvent A; acetonitrile; solvent B, water with 0.25% dicyclohexylammonium phosphate; flow rate 2 ml/min; temperature 40 °C; injection volume 5 μl; samples were analysed using a diode array detector. The following gradient programme was used:

	Min	%A	%B
	0	30	70
	5	50	50
	6	40	60
	7	30	70
Stop time	7		

Retention times (t_R) are in minutes.

Mass spectra were recorded with a Micromass Instruments LCT orthogonal time-of-flight mass spectrometer fitted with a Z-Spray electrospray ion source operating in negative mode at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data was stored in the continuum mode on a Micromass Instruments MassLynx data station utilizing Version 3.5 software pack. Infusion was at a rate of 20 μl/min with a Harvard Instruments syringe pump utilized for sample introduction.

Ultraviolet spectra were taken with a Camspec M350 Double Beam UV–Visible Spectrophotometer.

2.1. Phosphate buffer

Mixed phosphate buffer comprised potassium dihydrogen phosphate (two parts) and disodium hydrogen phosphate (one part).

DCT dyes were supplied by DyStar.

2.1.1. 4-m-Carboxypyridinium-6-p-sulphoanilino-s-triazine-2-oxide

To water (100 ml) was added nicotinic acid (4.06 g; 0.033 m) and the pH adjusted to 4.5. 2,4-dichloro-6-*p*-sulphoanilino-*s*-triazine [1] (10.3 g; 57% strength; 0.018 m) was added portionwise, at 33 °C, while maintaining the pH at 4.0–4.5 with 2 M sodium carbonate solution. After a few minutes a yellow colour formed. HPLC showed the steady disappearance of the starting DCT compound, t_R 1.69, and the formation of a new peak at t_R 0.67. The reaction was continued for 24 h and no other peak was observed by HPLC. The yellow suspension which resulted was filtered, the solid washed with acetone and dried to give the product (13.8 g). A small portion was lixiviated in cold water, filtered and oven dried at 85 °C. HPLC and TLC analysis showed the product to be identical to authentic material [1]; λ_{max} 270 nm (ε 3.0*10^4) and 315 nm (inflection; $\varepsilon = 3.9*10^3$). Found; C, 44.0; H, 2.3; N, 17.2; S, 7.2. $C_{15}H_{10}N_5O_6SNa$ requires C, 43.8; H, 2.5; N, 17.0; S, 7.8%.

2.1.2. 4-Pyridinium-6-p-sulphoanilino-s-triazine-2-oxide

To water (150 mls) was added 2,4-dichloro-6-*p*-sulphoanilino-*s*-triazine [1] (8.4 g; 57% strength; 0.015 m) and pyridine (3.6 g; 0.046 m) and the pH adjusted to 4.5. A yellow colour quickly developed. The reaction mixture was heated to 30 °C while maintaining the pH at 4.0–4.5 with 2 M

sodium carbonate solution. HPLC showed the steady disappearance of the DCT starting material, t_R 1.53, and the appearance of a new peak at t_R 0.51. A further addition of pyridine (2 g; 0.025 m) was added and the reaction allowed to stir overnight. Salt (25% w/v) was added, and the reaction mixture stirred for 1 h. The solid which separated was isolated by filtration, washed with water (40 ml) and with acetone (75 ml) and dried to give the product (3.9 g). HPLC showed a single peak at t_R 0.56, identical with authentic material [1]. Mass spectral analysis gave ions at m/z 344 $(M-H)^-$ (100), and 265 $(M-H-C_5H_5N)^-$ (5).

2.1.3. 4-m-Carboxypyridinium-6-(p-β-sulphatoethylsulphonyl)anilino-s-triazine-2-oxide

To *p*-aminobenzene-β-sulphatoethylsulphone (8.84 g; 95% strength; 0.03 m) in ice water (80 ml) was added 2 M sodium carbonate to give pH 4.5. The solution so formed was filtered though celite and then cooled to 0 °C in an ice bath. To this solution was added, dropwise, a solution of cyanuric chloride (5.7 g) in acetone (40 ml) while maintaining a temperature of 0–2 °C and pH 3.5–4.5. A white precipitate resulted and the reaction was continued for 2 h. HPLC showed the aromatic amine had disappeared. The reaction mixture was allowed to warm to RT, the pH adjusted to 6.5 with 2 M sodium carbonate solution and mixed phosphate buffer (2 g) added. The reaction was left to stir for 20 h, then filtered. The white solid so obtained, t_R 2.6, was added portionwise to a solution of nicotinic acid (4.08 g; 0.033 m) in water (150 ml) at RT and pH 4.5. The pH was maintained at 4.5 with 2 M sodium carbonate solution. A pale yellow colour developed and the reaction mixture was stirred for 25 h. HPLC showed a new peak at t_R 0.80, and the reaction to be virtually complete. The yellow suspension was filtered, the collected solid washed with acetone and dried at 40 °C to give the product (13.5 g) as a pale yellow solid. HPLC showed a single peak at t_R 0.80, and mass spectral analysis gave ions at m/z 496 $(M-H)^-$ (100) and 452 $(M-H-CO_2)^-$ (6). There was also a strong dimer ion at m/z 993 $(2M-H)^-$ (70).

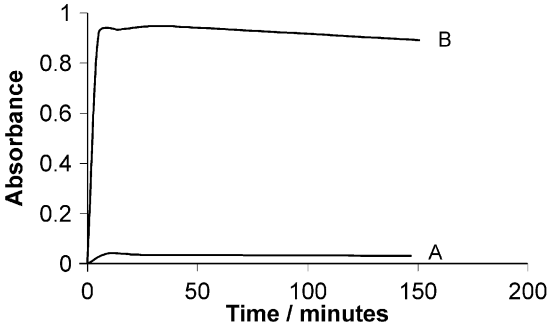


Fig. 1. Reaction of 6-chloro-4-*p*-sulphophenylamino-1,3,5-triazin-2(1H)-one (**I**, R = *p*-sulphophenyl) (A) and 4-*p*-sulphophenylamino-dichloro-*s*-triazine (No. 1, Table 1) (B) with nicotinic acid at pH 6.5–7.0.

2.1.4. 4-m-Carboxypyridinium-6-(1′-oxo-2′-phenylhydrazo-3′,6′-disulpho-1′,2′-dihydronaphth-8′-yl)amino-s-triazine-2-oxide

8-Dichlorotriazinylamino-2-phenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (Procion Red MX-5B; 12.5 g; 49.2% strength; 0.01 m) was dissolved in water (300 ml) and nicotinic acid (1.8 g; 0.015 m) added and the pH adjusted to 4.5. The reaction mixture, at 30 °C, was stirred for 24 h at pH 4–4.5 using 2 M sodium carbonate for adjustment. Salt (45 g) was added and the reaction mixture stirred for a further 2 h. The precipitate was isolated by filtration, washed with 10% brine and pulled down. The solid was dried in an electric oven at 65 °C to give the product (10.1 g). HPLC showed a single peak at t_R 0.81, and mass spectral analysis gave ions at m/z 638 $(M-H)^-$ (43), 594 $(M-H-CO_2)^-$ (15) and 515 $(M-H-ArN_2)^-$ (100).

2.1.5. 4-m-Carboxypyridinium-6-(1′-oxo-2′-o-sulphophenylhydrazo-3′,6′-disulpho-1′,2′-dihydronaphth-8′-yl)amino-s-triazine-2-oxide

8-Dichlorotriazinylamino-2-*o*-sulphophenylhydrazo-1-oxo-1,2-dihydronaphthalene-3,6-disulphonic acid (Procion Red MX-2B; strength approx. 50%; 14.2 g; 0.1 m) was dissolved in water (200 ml) and nicotinic acid (1.8 g; 0.015 m) added and the pH adjusted to 4.5. The reaction mixture was stirred for 24 h at pH 4–4.5 using 2 M sodium carbonate for adjustment. Salt (20 g) was added and the reaction mixture stirred for a further 1 h. The precipitate so formed was isolated by filtration,

washed with 20% brine and pulled down. The solid was dried in an electric oven at 65 °C to give the product (3.3 g). HPLC showed a single peak at t_R 1.38, and mass spectral analysis gave ions at m/z 718 $(M-H)^-$ (100), 674 $(M\text{-}H\text{-}CO_2)^-$ (9), 595 $(M-H-C_6H_5NO_2)^-$ (8).

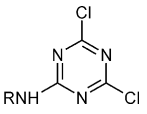
2.1.6. 4-m-Carboxypyridinium-6-[4′-(3″,6″,8″-trisulphonaphth-2″-yl)azo-3′-ureido]-phenylamino-s-triazine-2-oxide

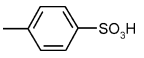
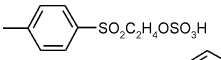
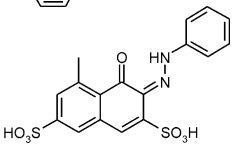
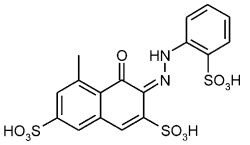
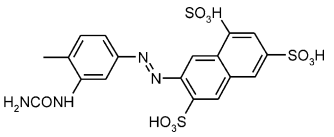
To 7-[(4′-dichloro-s-triazinylamino-2′-ureido)-phenylazo] - naphthalene - 1,3,6 - trisulphonic acid (Procion Yellow MX-3R; 50% strength; 4 g; 3.02 mmol) in water (100 ml) was added nicotinic acid (0.97 g; 7.9 mmol) and the pH adjusted to 4.5. The reaction mixture was stirred at RT for 3 days while maintaining the pH at 4.0–4.5 with 2 M sodium carbonate solution. Sodium chloride (6 g) was added to give an orange solid which was collected by filtration, washed with 10% brine, pulled down and oven dried at 85 °C to give the product (6.0 g). HPLC showed a single peak at t_R 1.28 (starting DCT t_R 2.99). Mass spectral analysis showed ions at m/z 760 $(M-H)^-$ (100), 716 $(M-H-CO_2)^-$ (10) and 637 $(M-H-C_6H_5NO_2)^-$ (25).

2.1.7. Relative reaction rates of 2,4-dichloro-6-p-sulphoanilino-s-triazine[1] and 6-chloro-4-p-sulphoanilino-1,3,5-triazin-2(1H)-one with nicotinic acid

2.1.7.1. Method. To deionised water (800 mls) was added, with stirring, the triazine derivative (0.2 mmoles), mixed phosphate buffer (5 g) and the solution heated to 30 °C. 2M sodium bicarbonate solution was added to give pH 6.5. Nicotinic acid (0.24 mmoles) was added and 2 M sodium bicarbonate solution added immediately to maintain the pH at 6.5–7.0. The reaction was followed by UV spectroscopy and measurements were taken at λ_{max} 315 nm.

Table 1
Dichlorotriazinyl compounds



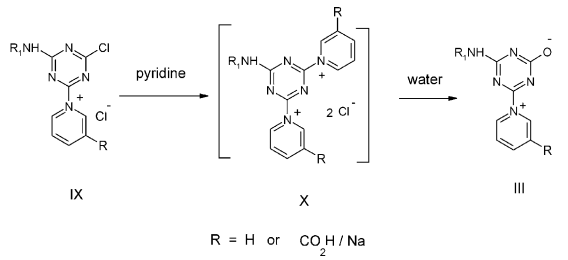
No	R
1	
2	
3	
4	
5	

3. Results and discussion

DCT compounds used for this work were either described in the literature [1,10] or were commercially available (Table 1).

Compounds **1** and **2** (Table 1) are colourless and reaction with either nicotinic acid or pyridine (compound 2 only), in acid medium, did not furnish the intense yellow coloration [6] (λ_{max} 440 nm; ε 6.9*10^4) associated with either the Zinke or the Fujiwara reactions. Accordingly, ring opening was not deemed to have occurred under the acid reaction conditions.

However, a pale yellow colour did develop as the reactions proceeded and the isolated products were pale yellow in colour. Compound **1** (Table 1) with nicotinic acid gave a solid which showed λ_{max} 270 nm ($\varepsilon = 3.0*10^4$) and 315 nm (inflection; $\varepsilon = 3.9*10^3$). This product was assigned structure (III; R = *p*-sulphophenyl; $R_1 = CO_2H$; Scheme 1) and was identical [1] to the product prepared by acid catalysed reaction of nicotinic acid with CTO compound (**I**; R = *p*-sulphophenyl). HPLC showed in both cases the transformation from DCT to triazine-oxide to be a very clean reaction, i.e. no by-products were detected. Similar results were obtained for the three DCT dyes (**3**, **4**, and **5**;



Scheme 5.

(Table 1), i.e. reaction with nicotinic acid gave only the triazine oxides. Scheme 3 shows three mechanistic pathways to the *s*-triazine-oxide, all proceeding via an initial quaternisation step to yield the pyridinium-*s*-triazinyl compound **IV** (Scheme 3). Previous literature on the reaction of pyridine and substitted pyridines with mono-, di- and trichloro-*s*-triazinyl compounds supports an initial quaternisation of the pyridine ring. Hydrolysis of the remaining chlorine atom of compound (**IV**; Scheme 3) leads directly to the formation of the s-triazine-2-oxide. Although this cannot be ruled out, pyridinium is generally regarded as a better leaving group [11,12] than chlorine when attached to a triazinyl ring. Replacement of the pyridinium ring in compound **IV** (Scheme 3) by water leads to a chlorohydroxy-*s*-triazine [6-chloro-1,3,5-triazin-2(1H)-one; Scheme 3] which is known to react with pyridines to furnish 4-pyridinium-*s*-triazine-oxides [1].

To illuminate, if this step is involved in the formation of 4-pyridinium-*s*-triazinyl-2-oxide, the DCT compound (No. **1**; Table 1) was reacted with nicotinic acid, at pH 6.5–7.0, to slow down any reaction of a chlorohydroxy-*s*-triazinyl species, as the latter is known [1] to be an acid catalysed reaction. Formation of the 4-pyridinium-*s*-triazinyl-2-oxide was followed by UV spectroscopy and was rapid. A repeat experiment, using the same concentrations and temperature, with the chlorohydroxy-*s*-triazine (**I**; R = *p*-sulphophenyl) was extremely slow and a comparison of reaction progress is shown in Fig. 1.

Accordingly, the reaction of a DCT compound, with pyridine or 3-carboxypyridine, does not proceed via a chlorohydroxytriazine intermediate. While the direct hydrolysis of the chlorotriazinyl species (**IX**) cannot be ruled out, it appears more likely that compound (**IX**) reacts with the best available nucleophile present, i.e. (substituted) pyridine, followed by collapse of the bis-pyridinium derivative (**X**) to furnish 4-(substituted)-pyridinium-*s*-triazine-2-oxides (Scheme 5).

4. Conclusion

Nicotinic acid and pyridine react with DCT compounds to furnish pyridinium or m-carboxy-pyridinium-*s*-triazine-2-oxides. A limited study suggests that a bis-pyridinium-*s*-triazinyl derivative is the penultimate species, and that chlorohydroxy-*s*-triazinyl [chloro-1,3,5-triazin-2(1H)-one] compounds are not intermediates in the reaction sequence.

References

[1] Renfrew AHM, Phillips DAS, Bates I. Dyes and Pigments 2003;59:99.
[2] Renfrew A, Hunter M. Reactive dyes for textile fibres. Society of Dyers and Colourists; 1999.
[3] Zinke Th. Ann Chem Liebigs 1904;330:361.
[4] Zinke Th, Heuser G, Möller W. Ann Chem Liebigs 1904; 333:296.
[5] Fujiwara K. Sitzber Abhandl Naturforsch Ges Rostock 1914;6:33.
[6] Burchfield HP, Schuldt PH. J Agric Food Chem 1958; 6(2):106.
[7] Saure S. Ber 1950;83:335.
[8] Menon MC, Bhola, Aggarwal JS. Chem Ind 1956;717.
[9] Tsujikawa T, Kakugaku Zasshi, 1965;85(9):846; Chem Abstr, 1966;64:735.
[10] Lewis DM, Yao J. J Soc Dyers Colourists 2000;116:285.
[11] Dawson TLJ. J Soc Dyers Colourists 1964;80:134.
[12] Siegel E. In: Venkataraman K, editor. The chemistry of synthetic dyes, vol. VI. New York and London: Academic Press; 1972. p. 149.