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Formation of 2-oxido-4-quaternary ammonium-*s*-triazinyl betaines from dichloro-*s*-triazinyl compounds: evidence for a bis-quaternary ammonium-*s*-triazinyl intermediate

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Abstract

The reaction of pyridine and nicotinic acid with 2,4-dichloro-6-*p*-sulphoanilino-*s*-triazine to furnish 2-oxido-4-quaternary ammonium-*s*-triazinyl betaines has been shown to be a general reaction for a range of aliphatic and heterocyclic tertiary bases. Triethylamine proved to be an exception, with failure to react being ascribed to steric factors. Reaction of with *N,N*-dimethylethanolamine in aqueous medium gave two main products. One was the expected betaine, 4-(*N,N*-dimethyl)-β-hydroxyethanaminium-6-sulphoanilino-*s*-triazinyl-2-oxide and the other 4-(*N,N*-dimethyl)-β-hydroxyethanaminium-2-(β-dimethylamino)-ethoxy-6-*p*-sulphoanilino-*s*-triazine (IX). Formation of the latter product is rationalised in terms of an internal aromatic nucleophilic substitution (Smiles rearrangement) of a highly electrophilic bis-quaternary ammonium triazinyl species. This highly reactive species has been isolated in an impure state, characterised by NMR, and rearranged to the triazinyl ether (IX) confirming both the Smiles rearrangement and the mechanistic pathway for the formation of triazinyl betaines from dichloro-*s*-triazinyl compounds and tertiary bases.

Keywords: Dichloro-*s*-triazine; *N,N*-dimethylethanolamine; Nicotinic acid; Betaine; Smiles rearrangement

1. Introduction

2-Oxido-4-*m*-carboxypyridinium-*s*-triazinyl betaines (I) are novel fibre reactive groups which can be prepared [1] from 6-chloro-1,3,5-triazin-2(1*H*)-ones (II) or, more conveniently, in a one step reaction [2] from dichloro-*s*-triazinyl (DCT) compounds (III) by reaction with nicotinic acid. Both reactions are best conducted in a weakly acidic medium (Scheme 1).

The mechanistic pathway from DCT compounds has not been elucidated. DCT compounds (III) undergo base-catalysed hydrolyses [3] to yield 6-chloro-1,3,5-triazin-2(1*H*)-ones (II)

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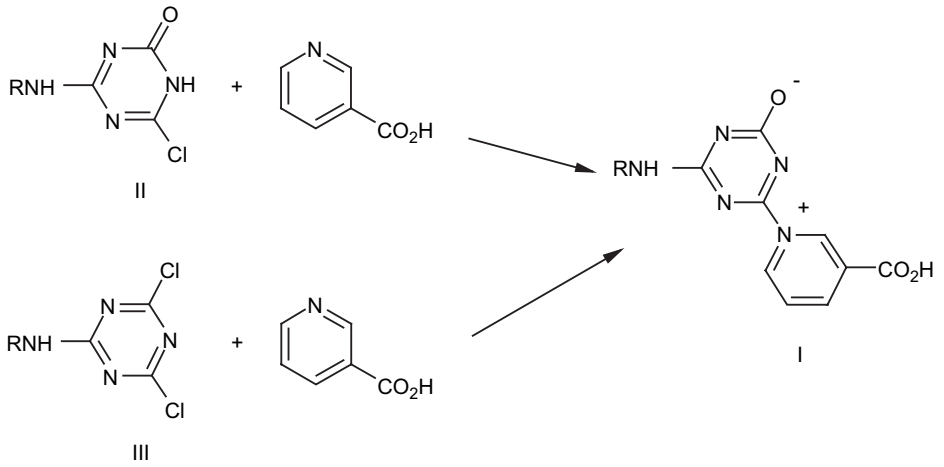


Scheme 1. Formation of triazinyl betaines.

(Scheme 2), but are relatively stable under weakly acidic conditions. Accordingly, formation of betaines (I) from DCT compounds (III) (Scheme 1) readily takes place under conditions which do not favour partial hydrolysis of dichlorotriazines.

Moreover, it has been shown [2] that, whereas nicotinic acid and 6-chloro-1,3,5-triazin-2(1*H*)-one (II; R = *p*-sulphoanilino), at pH 6.5–7.0, failed to react, the DCT compound (III), under the same conditions, was readily transformed into the betaine (I; R = *p*-sulphoanilino), thereby discounting path a (Scheme 3) as a reaction pathway. It has been postulated [2] that the formation of 2-oxido-4-*m*-carboxypyridinium-*s*-triazinyl betaines (I) from DCT compounds involves aromatic nucleophilic displacement of both chlorine atoms by nicotinic acid to form an unstable bis-quaternary-*s*-triazine (IV; path c; Scheme 3) which undergoes rapid hydrolysis in aqueous medium to give the product.

However, formation of betaine (I; R = *p*-sulphoanilino) via hydrolysis of the monochloro-monoquaternary ammonium intermediate (V; R = *p*-sulphoanilino; path b; Scheme 3) could not be eliminated as a possible pathway.

Further investigations to study the generality of this reaction, with alternative tertiary bases, have yielded supporting evidence for the intermediacy of a bis-quaternary-*s*-triazinyl species (IV; path c; Scheme 3).

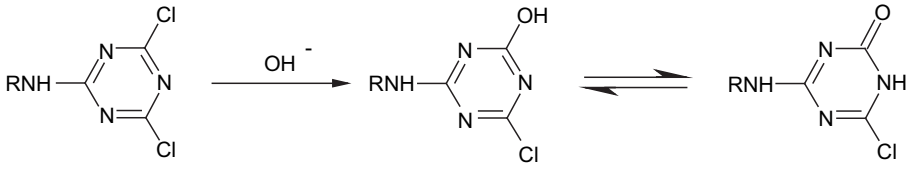
2. Experimental

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 LiChrocart 125-4 HPLC column cartridge; solvent A, acetonitrile; solvent B, water with 0.25% dicyclohexyl-ammonium 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	15	85
	8	50	50
	10	15	85
Stop time	10		

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 at 3 kV needle potential. Nitrogen was used as a drying and sheath gas. Data were 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.



Scheme 2.

LC-MS were run with a Micromass LCT TOF mass spectrometer. Separation was achieved with a 25 cm Hypersil BDS C18 (5 μm) column ex Thermo Life Sciences, Basingstoke, Hampshire, England, UK; solvent A, acetonitrile; solvent B, water; flow rate 1 ml/min; temperature 40 °C; injection volume 20 μl. The following gradient programme was used:

	Min.	% A	% B
	0	20	80
	16	80	20
	20	20	80
Stop time	20		

Retention times (t_R) are in minutes.

Mixed phosphate buffer comprised potassium dihydrogen phosphate (2 eq.) and disodium hydrogen phosphate (1 eq.).

^{1}H NMR spectra were recorded on a Bruker Avance at 300 MHz for ^{1}H and at 75.47 MHz for ^{13}C NMR in D_2O/NaOD (pH 9) unless otherwise stated. Chemical shifts, relative to TMS as the internal standard, are given in δ values. Coupling constants are given in Hertz. ^{13}C peaks were assigned by means of APT, HMQC and HMBC experiments. "d.i." denotes peaks with double intensity, "t.i." with triple intensity and q.i. with quadripole intensity.

2.1. 6-(N,N)-dimethylaminium-4-p-sulphoanilino-s-triazine-2-oxide (No. 1; Table 1)

To 6-*p*-sulphoanilino-*s*-dichlorotriazine [1] (17.3 g; strength 59.6%; 0.03 m), t_R 4.6, in water (50 ml) was added, with stirring, trimethylamine hydrochloride (7.0 g; strength 98%; 0.072 m). Sodium hydroxide solution (2 M) was added to give pH 7.5 and the suspension heated to 30 °C. The heat of the reaction caused the temperature to rise to 40 °C and 2 M sodium hydroxide was added to maintain a pH of 7.0–8.0. After 30 min the suspension dissolved and the solution so formed was filtered then allowed to stand for 2 h. The white precipitate which resulted was collected by filtration, lixiviated in acetone (150 ml) then refiltered and oven dried at 40 °C to give the product (9.1 g) as a white solid. HPLC showed a single peak, t_R 0.58, and mass spectrometry gave ions at m/z 324 $(M-H)^-$ (100) and 265 $(M-H-C_3H_9N)$ (10). There was also a dimer ion at m/z 649 $(2M-H)^-$ (1). ^{1}H NMR: δ 2.87 (s, 1H, NH), 3.31 (s, 9H, N–CH_3), 7.53 (d, 2H, ^3J = 8.5 Hz, ^{Ar}H), 7.68 (d, 2H, ^3J = 8.5 Hz, ^{Ar}H). ^{13}C NMR: δ 54.0 (N^+–CH_3, t.i.), 121.1 (^{Ar}CH, d.i.), 127.1 (^{Ar}CH, d.i.), 138.1 (^{Ar}C), 141.5 (^{Ar}C), 161.0, 166.4, 171.4.

Procedures for the following betaines were as described above.

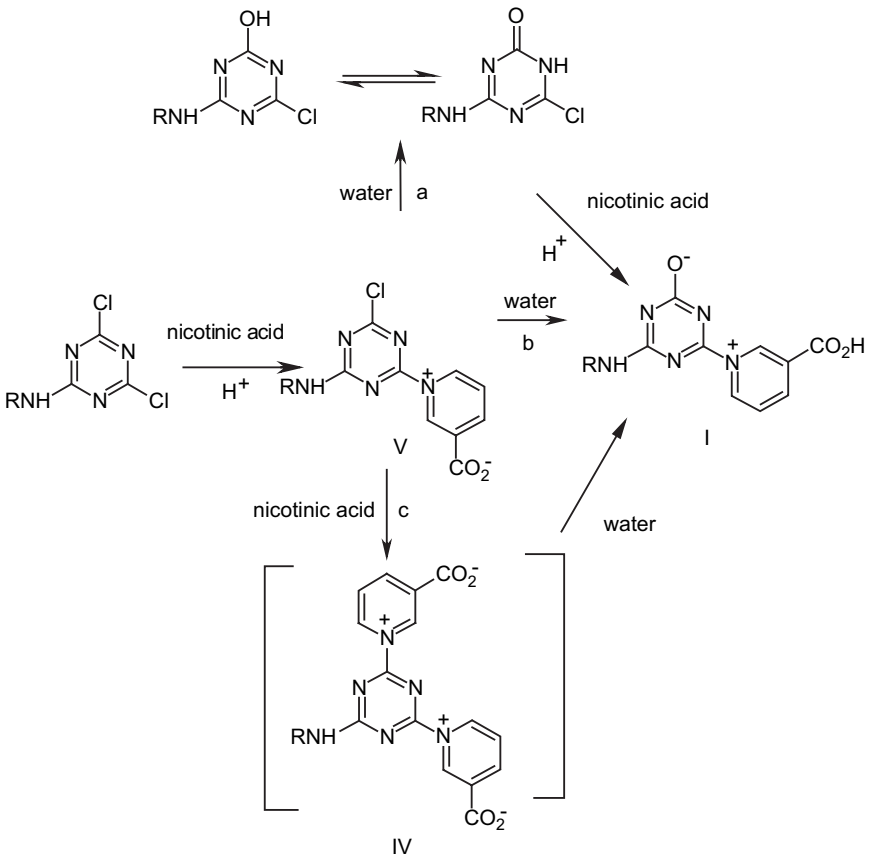
2.2. 6-N-methylpyrrolidinium-4-p-sulphoanilino-s-triazine-2-oxide (No. 3; Table 1)

4.3 g; HPLC showed a peak at t_R 0.57. Mass spectrometry gave ions at m/z 350 $(M-H)^-$ (100) and 265 $(M-H-C_5H_{11}N)^-$ (7). There was also a weak dimer ion at m/z 701 $(2M-H)^-$.

^{1}H NMR: δ 1.56 (m, 4H, CH_2), 2.21 (s, 3H, N–CH_3), 2.46 (m, 4H, N–CH_2), 2.80 (s, br, 1H, NH), 7.56 (dd, 2H, ^3J = 8.6 Hz, ^4J = 1.8 Hz, ^{Ar}H), 7.66 (d, 2H, ^3J = 8.6 Hz, ^4J = 1.8 Hz, ^{Ar}H). ^{13}C NMR: δ 26.3 (CH_2, d.i.), 44.5 (N^+–CH_3), 52.4 (N^+–CH_2, d.i.), 120.3 (^{Ar}CH, d.i.), 126.3 (^{Ar}CH, d.i.), 135.8 (^{Ar}C), 141.4 (^{Ar}C), 162.4, 165.8, 169.9.

2.3. 6-N-methylmorpholinium-4-p-sulphoanilino-s-triazine-2-oxide (No. 4; Table 1)

9.9 g; HPLC showed a single peak at t_R 0.56. Mass spectrometry gave ions at m/z 366 $(M-H)^-$



Scheme 3. Mechanistic pathways to triazinyl betaines from dichloro-*s*-triazines.

(100) and 265 $(M-H-C_5H_{11}NO)^-$ (23). There was also a weak dimer ion at *m*/*z* 733 $(2M-H)^-$. ^{1}H NMR: δ 2.21 (s, 3H, N–CH_3), 2.46 (t, 4H, ^3J = 4.6 Hz, N–CH_2), 3.26 (s, br, 1H, NH), 3.71 (t, 4H, ^3J = 4.6 Hz, O–CH_2), 7.67 (dd, 2H, ^3J = 8.8 Hz, ^4J = 1.9 Hz, ^{Ar}H), 7.75 (d, 2H, ^3J = 8.8 Hz, ^4J = 1.9 Hz, ^{Ar}H). ^{13}C NMR: δ 43.9 (N^+–CH_3), 53.0 (N^+–CH_2, d.i.), 65.3 (O–CH_2, d.i.), 119.7 (^{Ar}CH, d.i.), 125.3 (^{Ar}CH, d.i.), 135.2 (^{Ar}C), 141.2 (^{Ar}C), 165.7, 168.8, 168.9.1

Table 1
Reaction of DCT compound (III; R = *p*-sulphoanilino) with tertiary amines

No.	Amine	Product
1	Trimethylamine	Betaine
2	Triethylamine	No reaction
3	*N*-methylpyrrolidine	Betaine
4	*N*-methylmorpholine	Betaine
5	1,4-Diazabicyclo[2,2,2]octane	Betaine
6	Hexamethylenetetramine	Betaine
7	*N,N*-dimethylethanolamine	Mixture

2.4. 6-(1,4-Diaza-bicyclo[2.2.2]octanaminium)-4-p-sulphoanilino-s-triazine-2-oxide (No. 5; Table 1)

10.8 g; HPLC showed a single peak at t_R 0.53. Mass spectrometry gave ions at *m*/*z* 377 $(M-H)^-$ (100) and 265 $(M-H-C_6H_{12}N_2)^-$ (25). There were also dimer ions at *m*/*z* 777 $(2M-2H+Na)^-$ (4) and 755 $(2M-H)^-$ (3). ^{1}H NMR: δ 3.17 (s, 1H, NH), 3.19 (t, 6H, ^3J = 6.7 Hz, N–CH_2), 3.56 (t, 6H, ^3J = 6.7 Hz, N^+–CH_2), 7.47 (d, 2H, ^3J = 8.6 Hz, ^{Ar}H), 7.65 (d, 2H, ^3J = 8.6 Hz, ^{Ar}H). ^{13}C NMR: δ 44.3 (N–CH_2, t.i.), 52.2 (N^+–CH_2, t.i.), 120.0 (^{Ar}CH, d.i.), 126.3 (^{Ar}CH, d.i.), 137.0 (^{Ar}C), 140.8 (^{Ar}C), 165.3, 169.5, 176.1.

2.5. 6-(1,3,5,7-Tetraazatricyclo [3.3.1.1^{3,7}]decanaminium)-4-p-sulphoanilino-s-triazine-2-oxide (VII; No. 6; Table 1)

10.8 g; HPLC showed a single peak at t_R 0.54. Mass spectrometry gave a molecular ion at m/z 405 $(M-H)^-$ (100).

2.6. Reaction of N,N-dimethylethanolamine with 4-p-sulphoanilino-s-dichlorotriazine (No. 7; Table 1)

(a) To a suspension of 2,4-dichloro-6-*p*-sulphoanilino-*s*-triazine [1] (17.3 g; strength 59.6%; 0.03 m), t_R 4.6, in water (100 ml) at pH 6.6, was added dropwise over 30 min, with stirring, *N,N*-dimethylethanolamine (6 g; strength 99%; 0.067 m). A pH of 7.0–8.0 was maintained by either controlling the addition of tertiary amine or by addition of 2 M sodium carbonate solution. The temperature during the amine addition was kept between 20–26 °C and after 35 min a grey solution was given. The solution was stirred for a further 2 h then drowned slowly into ethanol (300 ml) to give a sticky grey solid. The solid was transferred to acetone (300 ml) and stirred for a further 30 min to give a free flowing suspension. The pale grey solid which resulted was isolated by filtration, washed with a little acetone and oven dried to give the product (11.6 g). HPLC showed peaks at t_R 0.54 (approx. 60%) and t_R 0.83 (approx. 40%). A mass spectrum of the mixture gave ions at m/z 425 $(M-H)^-$ (26) and 381 $(M-H-C_2H_4O)^-$ (12) consistent with a molecular formula of $C_{17}H_{26}N_6O_5S$ for the triazinyl ether (IX; Scheme 5). There were also ions at m/z 354 $(M-H)^-$ (25), 310 $(M-H-C_2H_4O)^-$ (18), and 265 $(M-H-C_4H_{11}NO)^-$ (100) consistent with $C_{13}H_{17}N_5O_5S$ for the triazinyl betaine (VIII; Scheme 5).

The sample was re-run by LC-MS in positive mode. The triazinyl betaine, t_R 4.15, showed ions at m/z 400 $(MNa+Na)^+$ (8), 378 $(M+Na)^+$ (10), 356 $(M+H)^+$ (100), and 311 $(M+H-C_2H_4O)^+$ (33). The higher molecular species (IX), t_R 4.20 showed ions at m/z 427 $(M+H)^+$ (8), 397 $(M+H-CH_2O)^+$ (33), 338 $(M+H-C_4H_{11}NO)^+$ (42) and 324 $(M+H-CH_2O-C_4H_{11}N)^+$ (100).

(b) The reaction was carried out as per method (a) using a mixture of mixed phosphate buffer and acetone (1:1) with tlc control to find the concentration maxima. Separation of the mixture was performed on basic aluminium oxide with acetone/DMF as eluant (2:1). NMR were taken in D_2O at pH 7, for compounds (VIII) and (IX) and in D_2O at pH 10 to follow the rearrangement of the bis-quaternary ammonium compound (XI).

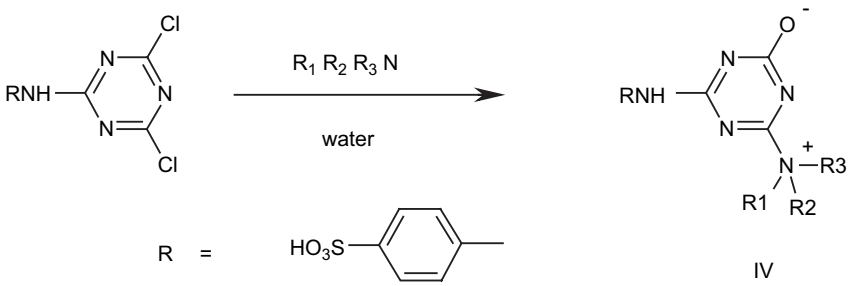
Triazinyl betaine (VIII); ^{1}H NMR: δ 3.46 (s, 6H, N^+-CH_3), 3.82 (t, 2H, ^3J = 4.2 Hz, N^+-CH_2), 4.04 (t, 2H, ^3J = 4.2 Hz, $O-CH_2$), 7.65 (dd, 2H, ^3J = 8.8 Hz, ^4J = 1.8 Hz, ^{Ar}H), 7.74 (d, 2H, ^3J = 8.8 Hz, ^4J = 1.8 Hz, ^{Ar}H). ^{13}C NMR: δ 51.3 (N^+-CH_3, d.i.), 60.6 (N^+-CH_2), 64.1 ($O-CH_2$), 119.2 (^{Ar}CH, d.i.), 125.3 (^{Ar}CH, d.i.), 135.8 (^{Ar}C), 141.3 (^{Ar}C), 164.1, 169.4, 170.0.

Triazinyl ether (IX); ^{1}H NMR: δ 2.21 (s, 6H, $N-CH_3$), 2.51 (t, 2H, ^3J = 4.8 Hz, $N-CH_2$), 3.54 (s, 6H, N^+-CH_3), 3.78 (t, 2H, ^3J = 4.8 Hz, $O-CH_2$), 3.80 (t, 2H, ^3J = 4.4 Hz, N^+-CH_2), 4.12 (t, 2H, ^3J = 4.4 Hz, $O-CH_2$), 7.52 (d, 2H, ^3J = 8.6 Hz, ^{Ar}H), 7.63 (d, 2H, ^3J = 8.6 Hz, ^{Ar}H). ^{13}C NMR: δ 44.1 ($N-CH_3$, d.i.), 52.5 (N^+-CH_3, d.i.), 53.6 ($N-CH_2$), 60.8 ($O-CH_2$), 63.4 (N^+-CH_2), 64.6 ($O-CH_2$), 119.4 (^{Ar}CH, d.i.), 125.5 (^{Ar}CH, d.i.), 135.2 (^{Ar}C), 142.0 (^{Ar}C), 162.4, 168.3, 175.4.

Bis-quaternary ammonium intermediate (XI); ^{1}H NMR: δ 3.46 (s, 12H, N^+-CH_3), 3.75 (t, 4H, ^3J = 4.3 Hz, N^+-CH_2), 4.14 (t, 4H, ^3J = 4.3 Hz, $O-CH_2$), 7.68 (d, 2H, ^3J = 8.4 Hz, ^{Ar}H), 7.82 (d, 2H, ^3J = 8.4, ^{Ar}H). ^{13}C NMR: δ 52.5 (N^+-CH_3, q.i.), 56.0 (N^+-CH_2, d.i.), 64.6 ($O-CH_2$, d.i.), 119.4 (^{Ar}CH, d.i.), 125.0 (^{Ar}CH, d.i.), 135.9 (^{Ar}C), 141.2 (^{Ar}C), 167.3, 172.6.

3. Results and discussion

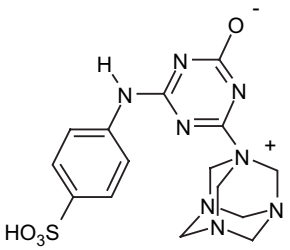
Unlike pyridine and nicotinic acid [2], reactions of the more basic aliphatic and heterocyclic tertiary amines, with the model DCT compound, were carried out at pH 7–8 and the derived products are listed in Table 1. Formation of



Scheme 4.

2-oxido-4-quaternary ammonium-*s*-triazinyl betaines (IV; Scheme 4) appears to be a general reaction although there was one exception. It has been noted previously [4], and ascribed to steric factors, that monochloro-*s*-triazinyl compounds fail to quaternise triethylamine. A similar explanation can be advanced for the model DCT compound.

R_1, R_2, R_3 (Scheme 4) may be (substituted) alkyl groups or may form part of a heterocyclic ring. The product (VII) formed from hexamethylenetetramine was characterised by mass spectrometry, but proved unstable. HPLC analysis after six weeks storage in the dark, at 20–25 °C, showed considerable decomposition.



VII

Of the tertiary bases which formed betaines with DCT compound (III; R = *p*-sulphoanilino), one amine, *N,N*-dimethylethanolamine, behaved differently from the others, giving a mixture of two main products.

Reverse phase HPLC showed product peaks at t_R 0.54 (~60%; and tentatively assigned to the triazinyl betaine) and an unknown band at t_R 0.83 (~40%). As HPLC of the starting DCT compound (III; R = *p*-sulphoanilino) gave a peak at t_R 4.6, the reduced retention time for both reaction products is in keeping with the formation of zwitterionic species and with the first eluted species being a triazinyl betaine (Section 2; see t_R values for related products). A mass spectrum of the mixture in negative mode (Fig. 1) showed an ion at m/z 354 $(M-H)^-$ consistent with 355 Da for the expected betaine (VIII; Scheme 5). There was also a higher molecular weight species at m/z 425 $(M-1)^-$ for a molecular mass of 426 Da consistent with a molecular formula of $C_{17}H_{26}N_6O_5S$, indicating that a stable reaction product was formed from 2 mole of *N,N*-dimethylethanolamine and 1 mole of the DCT compound. This stable zwitterionic compound is assigned the triazinyl ether (IX; Scheme 5) where the counter ion is SO_3^-.

Fig. 1 also shows the presence of an ion at m/z 283 $(M-H)^-$ for 284 Da. This is consistent for the presence of the triazin-2,4(1*H*,3*H*)-dione derivative (X) as a hydrolysis product of the triazinyl betaine (VIII).

In keeping with the other tertiary amines studied, betaine (VIII) was the expected product of reaction of DCT compound (III; R = *p*-sulphoanilino) and *N,N*-dimethylethanolamine. However, this amine also furnished the triazinyl ether (IX) as a major product and under conditions (20–26 °C; pH 7–8) unfavourable for deprotonation of the alcohol group and for conventional formation of ether (IX). For alcohols as nucleophiles, it is known that the rate of

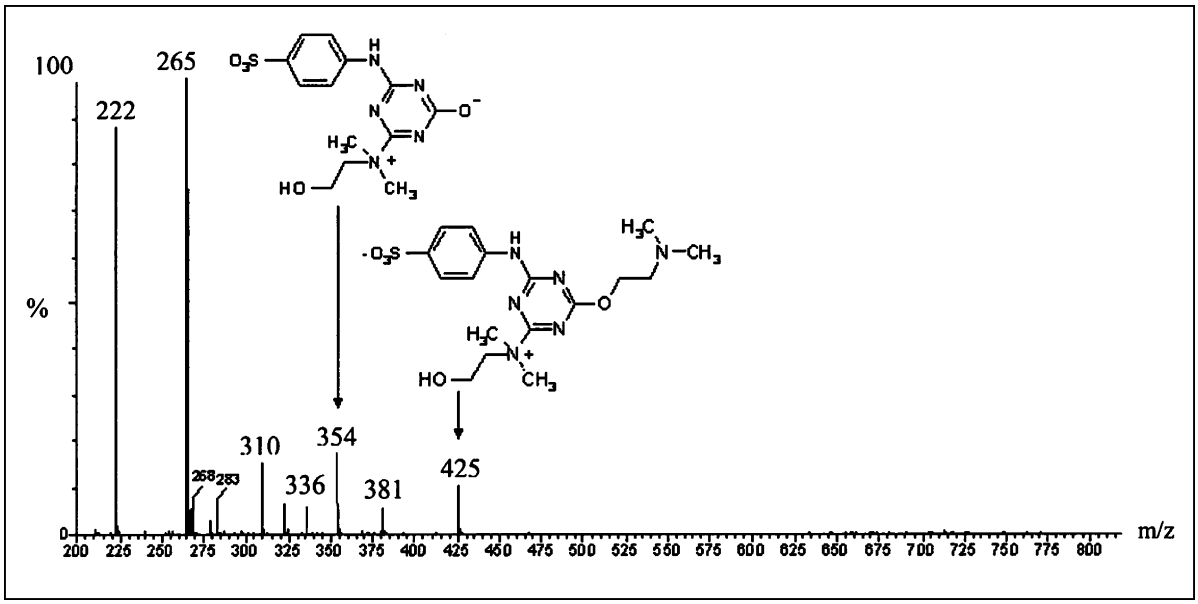
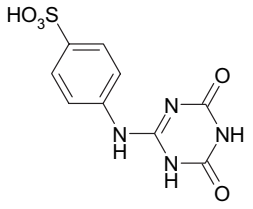


Fig. 1. Mass spectrum of the reaction mixture formed from *N,N*-dimethylethanolamine and 4-*p*-sulphoanilino-*s*-dichlorotriazine.

formation of a σ-complex in an S_NAr reaction [5] is linearly dependent on [RO^-].



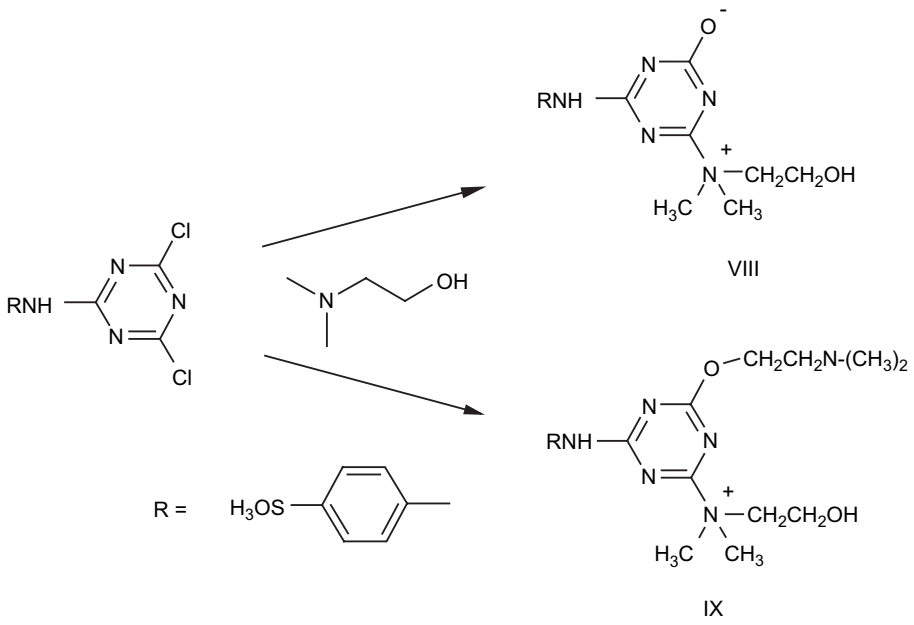
X

Moreover, running the aqueous reaction four times more dilute did not significantly alter the product ratio indicating that the ether was unlikely to be formed by direct competition of the alkoxyl group with water.

The origin of compound (IX; Scheme 5) is readily explained if a bis-quaternary ammonium intermediate (XI; Scheme 6) is involved in the reaction. An intramolecular S_NAr reaction (Smiles rearrangement) [6] of this activated heteroaromatic species would give product (IX). Such a highly electrophilic triazinyl intermediate, with both quaternary ammonium activating groups separated from the nucleophilic hydroxyl groups by two carbon atoms is ideally set up for such a reaction to occur. Generally, Smiles rearrangements require alkali to proceed. However, for this structure, the high reactivity of the bis-quaternary ammonium intermediate (XI; Scheme 6) renders unnecessary a deprotonation of the hydroxyl group. Only one quaternary ammonium group rearranges under the "neutral" conditions of the reaction since the electrophilicity of the triazinyl ring in compound (IX) is now reduced by the attached electron donating oxygen atom.

Confirmation of the proposed mechanism was achieved by NMR studies. Reaction of the DCT compound (III; R = *p*-sulphoanilino) with *N,N*-dimethylethanolamine was repeated in a mixed phosphate buffer/acetone solution (1:1). Samples were withdrawn at the beginning and at the end of the reaction and chromatographed, in turn, on basic aluminium oxide to separate the two stable components (VIII), and (IX) together with an impure sample of the unstable bis-quaternary ammonium species (XI), contaminated with betaine (VIII).

Quaternization of the nitrogen in *N,N*-dimethylethanolamine caused a strong downfield shift of the ^1H resonances. The methyl groups changed from ~2.2 ppm to ~3.5 ppm, the *N*-methylene groups from ~2.5 to ~3.8 ppm, and the *O*-methylene from ~3.8 to ~4.1 ppm. The ^{13}C



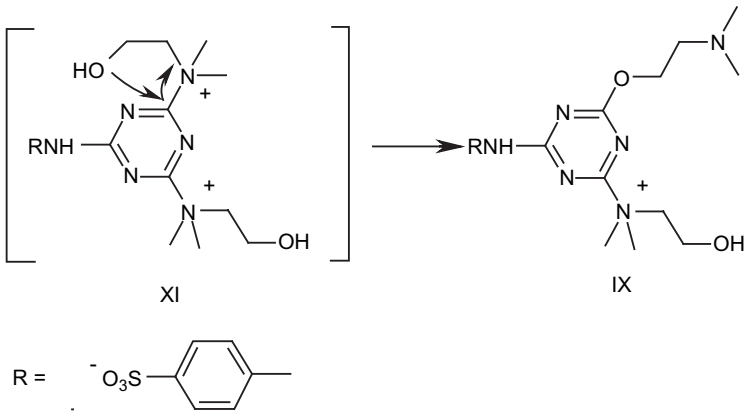
Scheme 5. Reaction of *N*,*N*-dimethylethanolamine with 4-*p*-sulphoanilino-*s*-dichlorotriazine.

resonances also were shifted downfield, e.g. the $N-CH_3$ from ~44 to 52 ppm.

While the intermediate (XI; Scheme 6) was both impure and unstable, undergoing change with time, it was nevertheless characterised by NMR. The two $-N^+-(Me)_2-CH_2-CH_2OH$ groups were equivalent as the molecule is symmetric and the triazine ring gave only two ^{13}C resonances for the same reason.

Furthermore, addition of NaOD to a solution of the unstable compound (XI), in an NMR tube, accelerated rearrangement to the triazinyl ether (IX), and allowed the reaction to be performed and followed in the NMR spectrometer.

Accordingly, study of the reaction of the model DCT compound (III; R = *p*-sulphoanilino) with *N*,*N*-dimethylethanolamine has furnished conclusive proof of the existence of a highly electrophilic bis-quaternary ammonium triazinyl intermediate. Such an intermediate can react with water to yield the triazinyl betaine (VIII) confirming mechanistic pathway c (Scheme 3). For this special tertiary



Scheme 6. Smiles rearrangement of the bis-quaternary ammonium triazinyl intermediate.

base, the reactive intermediate can also undergo a Smiles rearrangement to give the triazinyl ether (IX).

4. Conclusions

A range of aliphatic and heterocyclic tertiary bases have been shown to react with a model dichloro-*s*-triazinyl compound to give 2-oxido-4-quaternary ammonium-*s*-triazinyl betaines. While the reaction appears to be a general one, triethylamine proved to be an exception, and failure is ascribed to steric factors. Reaction with *N,N*-dimethylethanolamine in aqueous medium gave two main products. One was the expected betaine, 4-(*N,N*)-dimethyl-β-hydroxyethanaminium-6-sulphoanilino-*s*-triazinyl-2-oxide and the other 4-(*N,N*)-dimethyl-β-hydroxyethanaminium-2-(β-dimethylamino)-ethoxy-6-*p*-sulphoanilino-*s*-triazine. Formation of the latter product is rationalised in terms of an intramolecular S_NAr reaction (Smiles rearrangement), of a transient bis-quaternary ammonium triazinyl precursor. The highly reactive bis-quaternary ammonium compound (XI; Scheme 6) has been isolated in an impure state, characterised by NMR, and rearranged to the triazinyl ether (IX) confirming both the Smiles rearrangement and the mechanistic pathway for the formation of triazinyl betaines from dichloro-*s*-triazinyl compounds and tertiary bases.

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