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Two new triazinium perchlorates, **1** and **2**, readily lose perchloric acid, especially in the presence of a base to afford the corresponding anhydrobases. These are easily methylated but the product from **1** appears not to retain the original electronic configuration.

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In our continuing attempts to prepare potential anti-malarial target compounds we recently reported the synthesis of several new condensed 1,3,5-triazinium perchlorates from 1-chloroazainium or 1-chloro-2,4-diazainium salts, obtained from the reaction of dimethylcyanamide with phosphorus oxychloride-tertiary amide complexes or phosphorus oxychloride-secondary amide complexes, respectively [1,2]. It was shown that 1-chloro-1,3-bis(dimethylamino)-3-phenyl-2-azaprop-2-en-1-ylum perchlorate (**7**) reacted with 3-amino-1,2,4-triazole in refluxing acetonitrile to afford the fully conjugated salt, 4-dimethyl-2-phenyl-1,2,4-triazolo[4,3-*a*]-1,3,5-triazinium perchlorate **1**. Similarly 2-aminobenzimidazole gave 4-

dimethylamino-2-phenyl-1,3,5-triazino[1,2-*a*]benzimidazolium perchlorate **2** [3]. The same products were obtained from salts **8-11**.

The present investigation arose from the observation that salts **1** and **2** were rather unstable, especially in the presence of a base. Thus when a suspension of **1** or **2** in acetonitrile was stirred with 10% sodium hydroxide solution the corresponding anhydrobase **3** or **4**, was formed in high yield. The salts were easily regenerated by treatment with perchloric acid. Attempts to methylate the anhydrobases with the usual agents were unsuccessful; however, with methyl trifluoromethanesulfonate methylation proceeded remarkably well at room temperature to afford the methyl derivative **5** or **6** from **3** or **4**, respectively, as shown.

A comparative uv analysis of the perchlorate **1**, its anhydrobase **3** and the methyl-derivative **5** showed a shift in the  $\lambda_{\max}$  from 255 nm, for **1** and **3** to 280 nm, for **5**, suggesting that the same conjugated system is not preserved after methylation. This shift is rather unusual and no explanation is advanced for such electronic disfiguration except that methylation has occurred at a nitrogen atom other than the one that originally bore the hydrogen atom. In contrast, as expected, no significant change in uv absorption pattern was observed in the other series, as shown.

Finally biological activity has been established for these compounds by the Brine Shrimp Lethality bioassay [4].

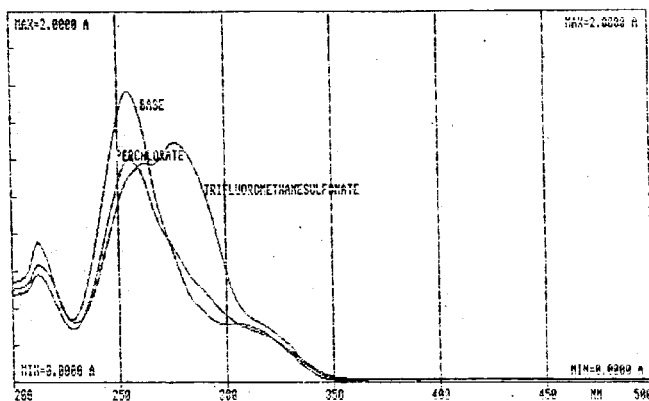
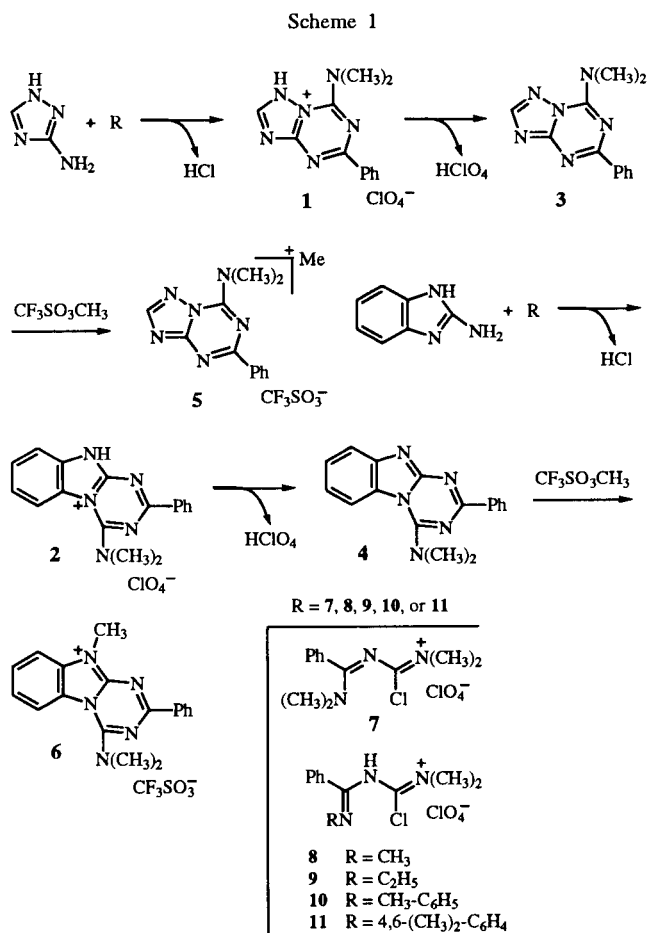


Figure 1. Comparative uv analysis of compounds **1**, **3** and **5**.

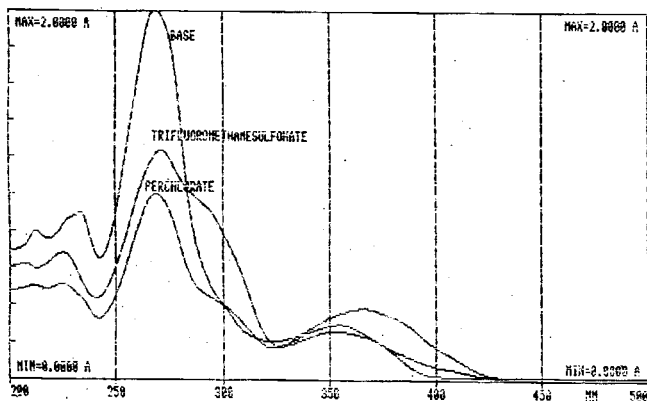


Figure II. Comparative uv analysis of compounds 2, 4 and 6.

## EXPERIMENTAL

Melting points were determined with a Gallenkamp electrically heated block and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer, incorporated with a data station, for nujol mulls on sodium chloride plates, unless stated otherwise. Ultraviolet spectra were recorded in the indicated solvent on a 402 spectrophotometer incorporated with a data station. The  $^1\text{H}$  nmr spectra were recorded on a Bruker WM 250 (250 MHz), a Nicolet NT 200 (200 MHz) or a Perkin Elmer R 32 (90 MHz) spectrometer. The data are recorded as the chemical shifts ( $\delta$ ) in parts per million (ppm) followed by integral, multiplicity and coupling constant (J in Hz) of the particular proton. Mass spectra were recorded with a micromass instrument 16F, incorporated with a data system Vg 2000, at 35 and 70 electron volts. Thin-layer chromatography (tlc) was conducted with Merck 60GF254 pre-coated silica gel plates. Drying and/or purification of organic solvents was done as described by Riddick and Bunger [5].

### General Procedure for the Preparation of the Anhydrobases 3 and 4.

A 10% aqueous solution of sodium hydroxide (5 ml) was added to a stirred suspension of the condensed 1,3,5-triazinium perchlorate (2 mmoles) in acetonitrile (10 ml). After 0.5 hours the resulting light yellow solution was poured into a large excess of crushed ice. When all the ice had melted the solid formed was collected and purified by crystallization from the solvent indicated.

The following anhydrobases were obtained:

#### 4-Dimethylamino-2-phenyl-1,2,4-triazolo[4,3-*a*]-1,3,5-triazine (3).

4-Dimethylamino-2-phenyl-1,2,4-triazolo[4,3-*a*]-1,3,5-triazinium perchlorate (1) [3] (0.05 g, 2 mmoles) gave 3 in 77% yield (0.27 g), mp 219–220° from ethyl acetate; uv:  $\lambda_{\text{max}}$  212 (18,000), 255 nm ( $\epsilon$  38,000); ir:  $\nu_{\text{max}}$  1619 (C=N), 1596 (C=C);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.70 (6H, s, NMe<sub>2</sub>), 7.50–7.60 (3H, m, Ph, J = 7.50 Hz), 8.23 (2H, t, Ph, J = 5 Hz); ms: *m/z* 240 (100) (M<sup>+</sup>), 225 (16), 210 (22), 77 (33).

*Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>: C, 59.98; H, 5.04; N, 34.98. Found: C, 60.00; H, 4.86; N, 35.20.

#### 4-Dimethylamino-2-phenyl-1,3,5-triazino[1,2-*a*]benzimidazole (4).

4-Dimethylamino-2-phenyl-1,3,5-triazino[1,2-*a*]benzimidazolium Perchlorate (2) [3] (0.67 g, 2 mmoles) gave 4 in 81% yield (0.54 g), mp 217–218° from ethyl acetate; uv:  $\lambda_{\text{max}}$  212 (23,000), 269 (58,000), 366 nm ( $\epsilon$  11,000); ir:  $\nu_{\text{max}}$  1628 (C=N), 1586 (C=C)

cm<sup>-1</sup>;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.29 (6H, s, NMe<sub>2</sub>), 7.39 (1H, t, J = 7.50, 15.00 Hz), 7.49–7.56 (4H, m, Ph), 7.77 (1H, d, Ph, J = 7.50 Hz), 7.92 (1H, d, Ph, J = 7.50 Hz), 8.64 (2H, dd, Ph, J = 7.50 Hz); ms: *m/z* 289 (100) (M<sup>+</sup>), 245 (16), 219 (22), 103 (14), 77 (33).

*Anal.* Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>5</sub>: C, 70.56; H, 5.24; N, 24.21. Found: C, 71.10; H, 5.32; N, 24.10.

### General Procedure for the Preparation of the Trifluoromethanesulfonates 5 and 6.

Methyl trifluoromethanesulfonate (0.69 g, 4 mmoles) was added dropwise to a solution of the anhydrobase (4 mmoles) in dichloromethane (15 ml). A white solid formed immediately. The reaction mixture was stirred for 0.5 hours. The solid was filtered off and washed with a little dichloromethane. It was collected and purified by crystallization from the solvent indicated.

The following trifluoromethanesulfonates:

#### 4-Dimethylamino-6-methyl-2-phenyl-1,2,4-triazolo[4,3-*a*]-1,3,5-triazinium Trifluoromethanesulfonate (5).

4-Dimethylamino-2-phenyl-1,2,4-triazolo[4,3-*a*]-1,3,5-triazine (3) (0.69 g, 4 mmoles) gave 5 in 95% yield (1.60 g), mp 253–254° from acetic acid; uv:  $\lambda_{\text{max}}$  275 nm ( $\epsilon$  62,000); ir:  $\nu_{\text{max}}$  1661, 1619 (C=N<sup>+</sup>), 1598 (C=C), 1222 cm<sup>-1</sup> (SO<sub>3</sub><sup>-</sup>);  $^1\text{H}$  nmr (DMSO-*d*<sub>6</sub>):  $\delta$  3.59 (3H, s, NMe), 3.83 (3H, s, NMe), 3.89 (3H, s, NMe), 7.61–7.72 (3H, m, Ph), 8.51 (2H, d, Ph, J = 7.50 Hz); ms: *m/z* 254 (100) (M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub>H), 239 (50), 225 (33), 77 (58).

*Anal.* Calcd. for C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>N<sub>6</sub>SO<sub>3</sub>: C, 41.58; H, 3.74; N, 20.78. Found: C, 41.77; H, 3.99; N, 20.98.

#### 4-Dimethylamino-7-methyl-2-phenyl-1,3,5-triazino[1,2-*a*]benzimidazolium Trifluoromethanesulfonate (6).

4-Dimethylamino-2-phenyl-1,3,5-triazino[1,2-*a*]benzimidazole (4) (0.79 g, 4 mmoles) gave 6 in 96% yield (0.76 g), mp 161–162° from acetic acid; uv:  $\lambda_{\text{max}}$  207 (28,000), 271 (56,000), 354 nm ( $\epsilon$  14,000); ir:  $\nu_{\text{max}}$  1642 (C=N<sup>+</sup>), 1594 (C=C), 1224 cm<sup>-1</sup> (SO<sub>3</sub><sup>-</sup>);  $^1\text{H}$  nmr (DMSO-*d*<sub>6</sub>):  $\delta$  3.34 (3H, s, NMe), 3.43 (3H, s, NMe), 4.09 (3H, s, NMe), 7.63–7.86 (5H, m, Ph), 8.04 (1H, d, Ph, J = 10.00 Hz), 8.13 (1H, d, Ph, J = 10 Hz), 8.60 (2H, d, Ph, J = 10.00 Hz); ms: *m/z* 304 (10) (M<sup>+</sup> – CF<sub>3</sub>SO<sub>3</sub>H), 289 (50), 275 (100), 77 (58).

*Anal.* Calcd. for C<sub>19</sub>H<sub>18</sub>F<sub>3</sub>N<sub>5</sub>SO<sub>3</sub>: C, 50.32; H, 4.00; N, 15.45. Found: C, 50.60; H, 3.99; N, 15.60.

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