## UNUSUAL DIMERIZATION OF 1-ETHYL-1,2,4-TRIAZINIUM SALTS

# INTO 4A,4B,9,10-TETRAHYDRO-1,3,6,8,8A,10A-HEXAAZAPHENANTHRENES

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<u>Summary</u>: 1- Ethyl-3-alkylthio-5-phenyl-1,2,4-triazinium tetrafluoroborates were found to undergo an unusual dimerization on treatment with triethylamine in methanol or ethanol solution. A mechanism for the formation of 4a,4b,9,10-tetrahydro-1,3,6,8,8a,10a-hexaazaphenanthrenes is proposed.

The chemistry of uncharged 1,2,4-triazines has been intensively studied for many decades.<sup>1-4</sup> Only a few papers report on behaviour of N-alkyl-1,2,4-triazinium cations.<sup>4-9</sup>

In the course of our systematic studies on reactions of N-alkylazinium cations with mono- and bifunctional nucleophiles 10 we have discovered a new type of dimerization in the series of azaaromatic compounds. The reaction of 1-ethyl-3-alkylthio-5-phenyl-1,2,4-triazinium tetrafluoroborates <u>la,b</u> with triethylamine in an ethanolic solution results in the formation of 4a,4b,9,10-tetrahydro-1,3,6,8,8a,10a-hexaazaphenanthrenes <u>2</u>a,b in 60 and 65 % yields, respectively (Scheme 1).



#### Scheme 1

Evidence for the structure of  $\underline{2}a$ , b is provided by the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy data. Chemical shifts and splitting patterns of the CH and CH<sub>2</sub> resonances in the <sup>1</sup>H NMR

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spectra of  $\underline{2}a$ , b correspond to the AA'X<sub>3</sub>X'<sub>3</sub> spin system, thus suggesting the CH<sub>3</sub>-CH-CH-CH<sub>3</sub> fragment is present in the molecules  $\underline{2}a$ , b (Figure 1).

In the coupled  $^{13}$ C NMR spectra of compounds 2a,b the CH<sub>3</sub> resonances appear as the double quartets and the CH resonances are multiplets due to coupling constants with protons of two methyl groups and methine hydrogen of the neighbouring CH group (Figure 1), as shown by selective decoupling experiments.



Figure 1. The  $^{n}J(C,H)$  coupling constants for the CH<sub>3</sub>-CH-CH-CH<sub>3</sub> fragment in the coupled  $^{13}C$  NMR spectrum of <u>2</u>a.

The presence of two dihydrotriazine rings in dimers  $\underline{2}a$ , b is also evident from the coupled  ${}^{13}C$  NMR spectra of compounds  $\underline{2}a$ , b in which the position of CH resonances in the field of 44-46 ppm indicates at the sp<sup>3</sup> character of these ring carbons while  ${}^{n}J(C,H)$  coupling constants are in full agreement with the  $C_{6}-C_{6}$ , dimeric structure (Figure 2). It should be noted that uncharged triazines are usually dimerized with the formation of the  $C_{5}-C_{5}$ , bond between two 1,2,4-triazine rings.<sup>1</sup>



Figure 2. The  $^{n}J(C,H)$  coupling constants for the dihydrotriazine ring carbon resonances in the  $^{13}C$  NMR spectrum of <u>2</u>a.

Although the  ${}^{1}$ H and  ${}^{13}$ C NMR spectral data revealed very important structural details of the dimeric molecules, an x-ray analysis of <u>2</u>a was indicated since the dimerization seemed to be very unusual and no examples of similar transformations of N-alkyl-azinium cations have so far been reported in the literature. The x-ray crystallography data for the compound <u>2</u>a proved unequivocally its hexaazaphenanthrene structure.<sup>11</sup>

Several mechanisms for the dimerization reaction can be advanced. We believe that the most plausible one involves the formation of biradicals  $\underline{6}$  as the key intermediates. The reaction is supposed to be initiated by deprotonation of 1-ethyl-1,2,4-triazinium salts 1 followed by cyclization of unstable ylides  $\frac{4}{2}$  into azirinotriazines 5. A similar process leading to the formation of azirinopyridazines was shown to occur in the reaction of 1-methylpyridazinium salts with bases. <sup>12</sup> However, attempts to detect the proposed intermediates 5by  ${}^{1}$ H NMR have failed. In examining the reaction mixtures in CD<sub>2</sub>OD at temperatures from -40<sup>0</sup> to +20 °C we have found that 1-ethyl-1,6-dihydro-6-methoxy-1,2,4-triazines 3a,b are immediately formed when 1-ethyl-1,2,4-triazinium salts <u>l</u>a,b are dissolved in CD<sub>2</sub>OD in the presence of triethylamine (2 eqv.). The 1,6-dihydro structure of G-adducts 3a,b is evident from strong upfield shifts for the H-6 resonance signals (5.90 and 5.82 ppm for the compounds  $\underline{3}a$  and  $\underline{3}b$  respectively). Other spectral parameters of **G**-adducts  $\underline{3}a$ , b are also in good agreement with the <sup>1</sup>H NMR spectral data for the alkoxy adducts of N-ethyl-1,4-diazinium cations. <sup>13</sup> The adducts 3a,b are comparatively stable at low temperatures and no trace of dimers 2a,b could be detected by  ${}^{1}$ H NMR below 0  ${}^{\circ}$ C. Standing solutions at room temperature results in the disappearance of the methoxy adducts <u>3</u>a,b with simultaneous increase of signals arising from the dimers 2a,b (Scheme 2).



Scheme 2

Experimental part. Dry triethylamine (2.0 g, 2.75 ml, 20 mmol) was added dropwise to a suspension of 1-ethyl-3-methylthio-5-phenyl-1,2,4-triazinium tetrafluoroborate <u>la</u> (3.2 g, 10 mmol) in 10 ml of anhydrous ethanol and the reaction mixture was kept at room temperature for 15 hours. A precipitate obtained was filtered off and recrystallized from anhydrous ethanol to yield 1.39 g of <u>2a</u> as red needles with m.p. 149-150  $^{\circ}$ C (60 %). <sup>1</sup>H NMR in CDCl<sub>3</sub>: 1.51 (6H, m, two methyl groups), 2.53 (6H, s, two methylthio groups), 3.76 (2H, m, H-10 and H-11), 5.21 (2H, s, H-4a and H-4b) and 7.1-7.6 ppm (10H, m, two phenyl groups). <sup>13</sup>C NMR in CDCl<sub>3</sub>: 13.66 (two methylthio groups), 16.10 (two methyl groups), 45.14 (C-4a and C-4b), 58.65 (C-10 and C-11), 127.47, 128.13, 132.17 and 133.93 (two phenyl groups), 151.50 (C-2 and C-7) and 161.7 ppm (C-4 and C-5).

The same procedure was used to convert 3-benzylthio-1-ethyl-5-phenyl-1,2,4-triazinium tetrafluoroborate <u>1b</u> into the dimer <u>2b</u>, m.p. 133-134<sup>0</sup>, yield 65 %. <sup>1</sup>H NMR in CDCl<sub>3</sub>: 1.21 (6H, m, two methyl groups), 2.95 (2H, m, H-10 and H-11), 4.15 (2H, d) and 4.37 (2H, d) (two S-CH<sub>2</sub>- groups, <sup>2</sup>J= 14.3 Hz), 4.75 (2H, s, H-4a and H-4b) and 7.1-7.6 ppm (2OH, m, 4 phenyl groups). <sup>13</sup>C NMR in CDCl<sub>3</sub>: 15.77 (two methyl groups), 34.81 (two SCH<sub>2</sub>- groups), 44.68 (C-4a and C-4b), 58.45 (C-10 and C-11), 127.18, 127.45, 127.51, 127.64, 128.53, 129.09, 129.31, 132.28, 132.66, 133.98, 138.18 (4 phenyl groups), 149.87 (C-2 and C-7) and 161.81 ppm (C-4 ang C-5). <sup>14</sup>

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