# PHOTOINDUCED FRAGMENTATION OF PYRIDO[2,1-f]-as-TRIAZINIUM-4-OLATE AND ITS BENZOLOGUE. A CONTRIBUTION TO THE MECHANISM OF CURTIUS REARRANGEMENT[1]

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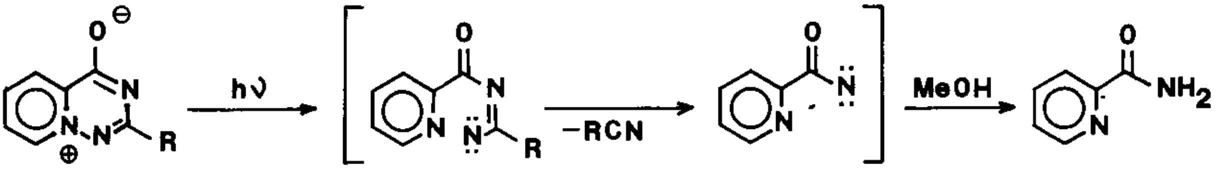
Abstract —— The zwitterionic pyrido[2,1-f]-as-triazinium-4-olates (1a-b) and as-triazino[6,1-a]isoquinolinium-1-olate (10) were photolysed to give acid amides (5) and (11), respectively. Formation of 5 through acylnitrene (4) was supported in separate experiment.

Numerous publications deal with the photochemical behaviour of five-membered betaines,[2] however, the photochemistry of six-membered zwitterions has been studied to a lesser extent.[3-8]

The photolysis of s-triazolopyridazinium-4-olates was earlier reported[9] and it was established that, upon the photolysis in methanol, opening of the pyridazine ring proceeded via the formation of an intermediate diaziridine ring and, subsequently, 3-aminotriazolo derivatives were formed.



1a,b

| | R |
|---|---|
| a | H |
| b | $C_6H_5$ |

2a,b

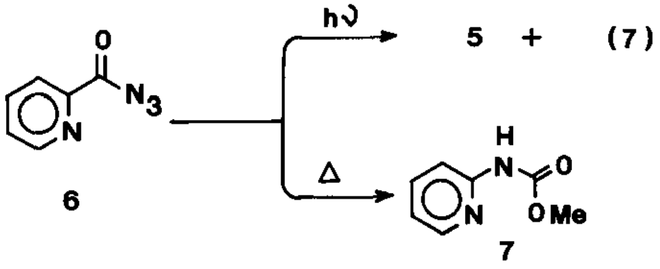
3a,b

4

5

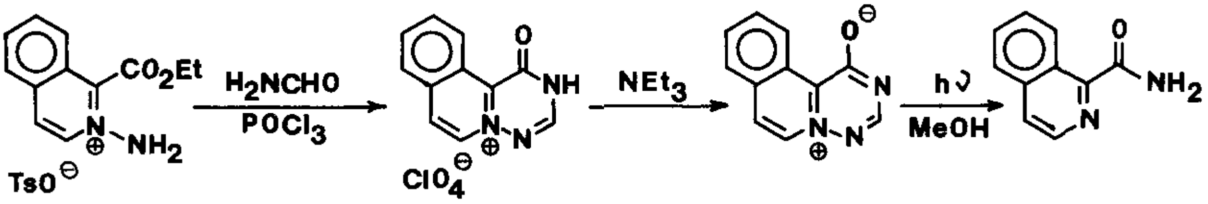
As a continuation of our investigations concerning the synthesis and reaction of pyrido [2,1-f]-as-triazinium-4-olates (1a-b)[10,11] we examined the photochemical behaviour of these zwitterionic compounds. The photolysis of the 4-olates (1a-b) (2 g of each) was performed in methanol (600 ml) with a medium pressure mercury lamp (750 W, 1.5 h, 20°C) immersed into the solution. A work-up of the photolysed solution by column chromatography ($Al_2O_3$; ethyl acetate : methanol = 95:5) afforded 2-pyridinecarboxamide (5)[12a] (58 and 60%, respectively).

In the case of 1a, the formation of HCN was detected[12b] and in the reaction of 1b ($R=C_6H_5$) benzonitrile (3b) was isolated in 30% yield. Their formation allows to propose a possible mechanism for the photoinduced process: a fission of the N-N bond[13] by electronical excitation takes place followed by elimination of RCN (3a-b) from nitrenes (2a-b) to give the same acylnitrene (4) which is finally stabilised by hydrogen-abstraction from the solvent yielding 2-pyridinecarboxamide (5).



The supposed existence of 4[14a] was supported by the photolysis of picolinoyl azide (6)[14b] which is also a possible source of 4. Thus, azide (6) when photolysed under the same conditions described above, afforded the amide (5) as major product (23%) and urethane (7)[15] as minor product (11%). However, the latter compound (7) was the only product (75%) when 6 (0.7 g) was refluxed in methanol (70 ml; 4.5 h).

As a further example, we synthesized the as-triazino[6,1-a]isoquinolinium-1-olate (10) (one of the possible three benzologues of olate (1a)) to extend our studies. Thus, 2-amino-1-ethoxycarbonylisoquinolinium tosylate (8)[16] was treated with formamide in the presence of phosphorous oxychloride (see procedure given for 1a;[10] CAUTION: HCN gas evolution!) to afford 1(2*H*)-oxo-*as*-triazino[6,1-*a*]isoquinolinium perchlorate (9)[17] in 65% yield. This salt was deprotonated by triethylamine to give 1-olate (10)[18] in 70% yield.



8 9 10 11

The zwitterionic system (10) was photolysed under the same reaction conditions as given for 1a-b to afford 1-isoquinolinecarboxamide (11) in 52% yield (mp 169-171°C; lit.,[19] mp 168-169°C). The reaction proceeded much slower (within 8 h).

The uv spectra of olate (10) and product (11) differ from each other significantly (Figure 1), therefore the photolytic decomposition can be followed by uv-maxima (Figure 2). On this basis, the overall quantum yield was estimated by spectroscopic measurement[20] and proved to be $\Phi = 3.1 \times 10^{-3}$ (± 5%). This value was found to be stable throughout the photolysis. To the best of our knowledge these findings represent the first photoinduced fragmentation of cyclic zwitterionic systems which - unlike other cyclic zwitterions - did not start with rearrangement but with direct ring opening.

The results of the photolysis of picolinoyl azide (6) and bicyclic olates (1a-b) allow to make a concluding remark on the mechanism of the Curtius rearrangement. Lwowski's study[21] showed that the Curtius rearrangement of the photolysis of pivaloyl azide could not involve any nitrene intermediate and revealed two simultaneous reaction pathways: (i) formation of isocyanate ("Curtius" and subsequent products), and (ii) formation of a nitrene intermediate and subsequent products which are, however, different from those formed through path (i).

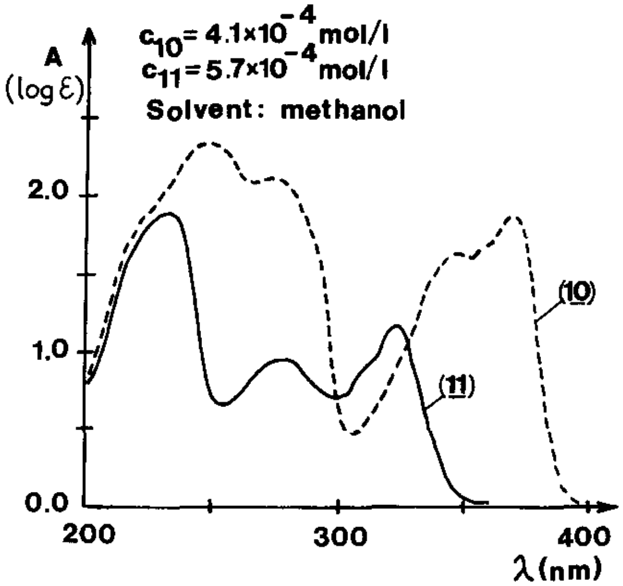


Figure 1. Uv spectra of as-triazino[6,1-a]isoquinolinium-1-olate (10) (--) and 1-isoquinolinecarboxamide (11) (—)

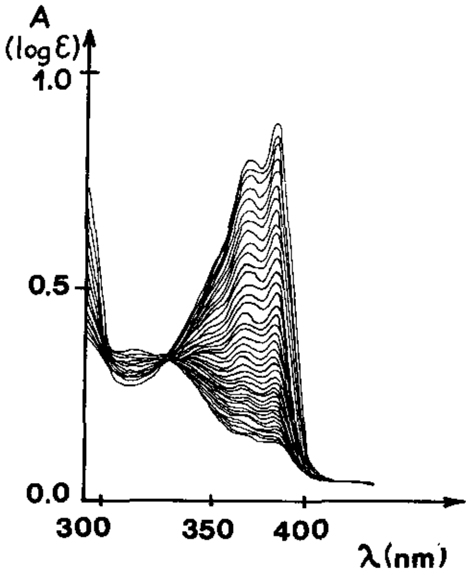


Figure 2. Change of the uv spectrum of 10 in the course of photolysis recorded in 15 min intervals (Methanol, $C_o = 7.1\times10^{-5}$ mol.l$^{-1}$, T = 20°C)

Similarly, in case of the photolysis of picolinoyl azide (6) we observed the formation of two compounds: (i) N-2-pyridylmethylurethane (7) as the product of reaction of 2-pyridylisocyanate (the result of the Curtius rearrangement) with methanol; and (ii) picolinoyl amide (5) which was obviously formed in reaction of the nitrene intermediate (4) and methanol. Since the photolysis of olates (1a-b) led to the same picolinoyl amide (5) and gave - unlike the analogous reaction of azide (6) - no "Curtius" product (7), we believe that these findings provide a novel support of the synchronous mechanism of the Curtius rearrangement involving no nitrene intermediate as suggested by Lwowski.

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15. mp 132-133$^{o}$C (methanol). Spectral data of 7: Ir (KBr): 3180, 3130, 3050, 2950, 2820, 1720, 1580, 1530, 1420, 1300, 1210 cm$^{-1}$; $^{1}$H nmr ($CDCl_3$): $\delta$ 10.60 (s, 1H, NH); 8.41 (d, $J_{5,6}$ = 4.8 Hz, 1H, H-6); 8.13 (d, $J_{3,4}$= 7.8 Hz, 1H, H-3); 7.72 (dd, $J_{3,4}$ = 7.8 Hz, $J_{4,5}$ = 7.0 Hz, 1H, H-4); 7.00 (dd, $J_{4,5}$ = 7.0 Hz, $J_{5,6}$ = 4.8 Hz, 1H, H-5); 3.88 (s, 3H, $CH_3$).

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17. All isolated compounds gave satisfactory elemental analyses, mp 272-274$^{o}$C (from acetonitrile—ethyl acetate). Spectral data of 9: Ir (KBr): 3080, 3050, 3040, 2750, 2650, 1720, 1640, 1610, 1590, 1070 cm$^{-1}$; $^{1}$H nmr (TFA): $\delta$ 9.10 (d, $J_{6,7}$ = 6.6 Hz, 1H, H-6); 8.82 (d, $J_{6,7}$ = 6.6 Hz, 1H, H-7); 8.80 (s, 1H, H-3); 8.60-8.20 (m, 4H, H-8,9,10,11).

18. mp 199-201$^{o}$C (acetonitrile). Spectral data of 10: Ir (KBr): 3120, 3090, 3070, 3040, 3010, 1640, 1615, 1550, 1510, 1490, 1450 cm$^{-1}$; $^{1}$H nmr (DMSO-$d_6$): $\delta$ 8.96 (d, $J_{6,7}$ = 6.8 Hz, 1H, H-6); 8.75 (s, 1H, H-3); 8.66 (d, $J_{6,7}$ = 6.8 Hz, 1H, H-7); 8.55-8.10 (m, 4H, H-8,9,10,11).

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