N-Quaternary Compounds. Part 52.[1] Photochemically Induced Valence Bond Isomerism and Rearrangement to Pyridinones of Thiazolo[3,2-*a*]-pyridinium-8-olate Derivatives

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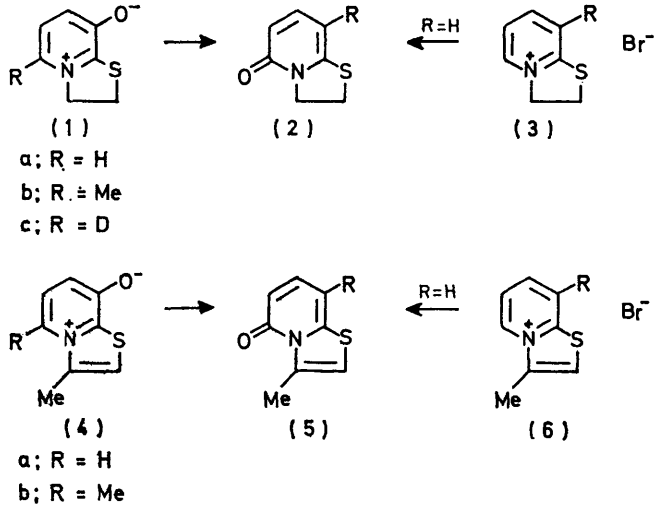
Irradiation of derivatives of thiazolo[3,2-*a*]pyridinium-8-olate with a medium pressure Hg lamp resulted in rearrangement to derivatives of the isomeric thiazolo[3.2-*a*]pyridin-5-ones. Irradiation at 350 nm of 5-methyldihydrothiazolo[3.2-*a*]pyridinium-8-olate gave the valence isomeric structure 6-methyl-2-thia-5-azatricyclo-[4.3.0.0^{1,5}]non-7-en-9-one which on further irradiation with the medium pressure Hg lamp yielded the corresponding rearranged dihydrothiazolo[3.2-*a*]pyridin-5-one.

IRRADIATION at 350 nm of *N*-phenylpyridinium-3-olate has yielded the valence isomeric 6-phenyl-6-azabicyclo-[3.1.0]hex-3-en-2-one besides dimeric products.[2] Irradiation of *N*-phenylpyridinium-3-olates using a medium pressure Hanovia Hg lamp and Pyrex filter, however, gave the isomeric *N*-phenyl-2-pyridone as the major product;[3] the 2-pyridone was not found after irradiation at 350 nm.[2] We herein report on the products formed on irradiation of thiazolo- and dihydrothiazolo-[3,2-*a*]pyridinium-8-olates.



(1) (2) (3)
a; R = H
b; R = Me
c; R = D

(4) (5) (6)
a; R = H
b; R = Me

SCHEME 1

The betaines (1) and (4) in ethyl acetate or acetonitrile were irradiated for 2—4 h using a medium pressure Hanovia Hg lamp (major u.v. bands at 313 and 366 nm) and Pyrex filter. The major reaction product was isolated by chromatography on silica gel. The product from 5-methyldihydrothiazolo[3,2-*a*]pyridinium-8-olate (1b) displayed i.r. absorption at 1 660 cm^{-1} in agreement with the lactam formulation (2b). The ^{1}H n.m.r. spectrum showed pyridine protons at δ 6.20 and 7.11 with *J* 8.5 Hz; the strong coupling is consistent with vicinal βγ-protons. The ^{13}C n.m.r. resonances were also in agreement with structure (2b): δ 28.2 (C-2), 51.3 (C-3), 161.8 (C-5), 114.9 (C-6), 142.5 (C-7), 109.0 (C-8), 145.0 (C-8a), and 17.7 p.p.m. (5-CH_3). The relative chemical shifts for the carbon atoms in the pyridine ring correspond well to the ^{13}C shifts reported for 2-pyridone.[4] The product was low melting (35—37 °C) and was a trihydrate in the crystalline state. *X*-Ray analysis confirmed the assigned structure (2b); an unusual feature is that the carbonyl oxygen atom in the crystalline trihydrate of (2b) acts as an acceptor for two hydrogen bonds.[5] The molecule is planar except for C-2 which is 0.42 Å out-of-plane in agreement with the geometry of other dihydrothiazolo[3,2-*a*]pyridinium derivatives.[5]

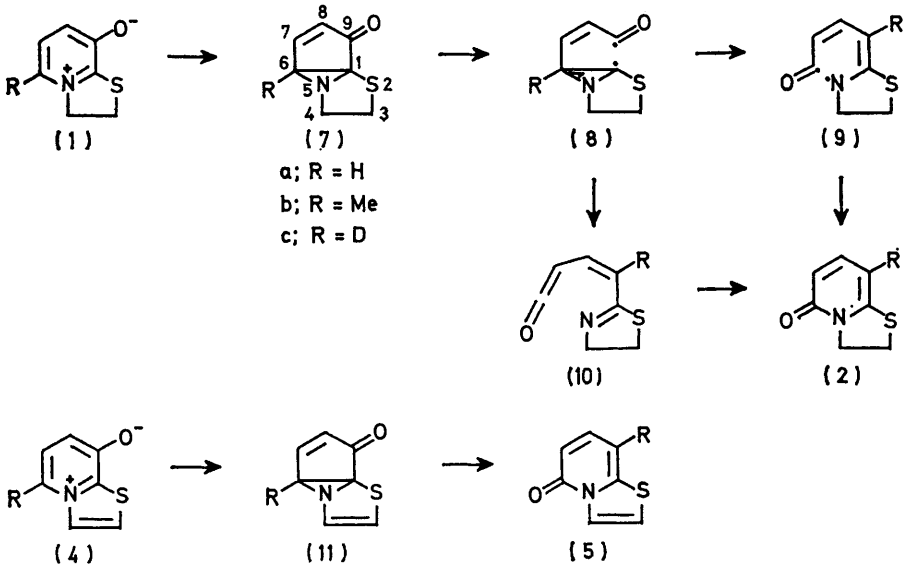
The product from irradiation of the parent betaine was by analogy shown to be the corresponding pyridinone (2a) by comparison with an authentic specimen prepared by oxidation of the corresponding cation (3a) using potassium hexacyanoferrate(III).[6]

Irradiation of the thiazolo[3,2-*a*]pyridinium-8-olates (4) gave the same type of pyridones (5) according to spectroscopic data. Thus the ^{13}C n.m.r. resonances for the ring carbons in the product from (4b) were δ 106.1 (C-2), 140.0 (C-3), 162.7 (C-5), 111.2 (C-6), 139.1 (C-7), 107.8 (C-8), and 147.5 p.p.m. (C-8a). The assignment of chemical shifts to the thiazole carbons is in accordance with literature data on thiazoles.[7] The assignment of structure (5a) to the product from (4a) was also verified by comparison with an authentic specimen prepared by potassium hexacyanoferrate(III) oxidation of the corresponding cation (6a).

A comparison of the isomer pairs (1b) and (2b), and of (4b) and (5b), respectively, shows that the net effect of the photolytic rearrangement corresponds to an interchange of the 5- and 8-substituents. The same positional interchange has also been demonstrated for (1a). This was done by irradiation of the corresponding 5-deuterio derivative (1c).[6] The ^{1}H n.m.r. spectra of the product showed two vicinal pyridine protons at δ 6.20 and 7.22 which could be assigned to H-6 and -7, respectively ($J_{6,7}$ 8.5 Hz). In the alternative 6-D isomer H-8 was found at δ 6.07 and H-7 at 7.22 ($J_{7,8}$ 7.5 Hz). Hence the photolysis product from (1c) must be (2c).

The extensive rearrangement can be rationalised by intermediate formation of a photolabile valence isomer (7) and (11). This corresponds to a photochemically allowed disrotatory ring closure in analogy with the formation of 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one from *N*-phenylpyridinium-3-olate on irradiation,[2] as well as to the photochemically reversible isomerism between 1-aryl-1a,6a-dihydroindeno[1,2-*b*]azirin-6(1*H*)-ones and 2-aryl-4-isoquinolinium-4-olates,[8] and imide

analogues.[9] In the related oxygen analogue system irradiation of polyphenyl substituted pyrylium-3-olates readily yielded the corresponding valence isomers in a reversible manner,[10,11] whereas irradiation of 2,3-epoxyindanone gave mainly isocoumarin.[12] 4-Pyrones are photoisomerised to 2-pyrones, and it has recently been shown that 2,5-dimethylcyclopentadienone epoxide is an intermediate in the isomerism of 3,5-dimethyl-4-pyrone to 3,6-dimethyl-2-pyrone.[13] A similar intermediate has been postulated in photochemical rearrangements of 4- to 2-pyridones, but the rearrangement of pyridones occurs less readily than for the oxygen analogue.[14]



SCHEME 2

Intermediate formation of a photolabile isomer (7) and (11) seems possible in view of the reports in the literature of related reactions as briefly reviewed above. Ring opening of the valence isomer and recyclisation in a different manner are indicated in Scheme 2. The species undergoing recyclisation may either by drawn as a biradical (9) or perhaps better as a keten (10).

In an effort to seek support for the intermediacy of a valence isomer compounds (1b) and (4a) were also irradiated at 350 nm using a Rayonet reactor (RPQ-100). The thiazole (4a) gave only the pyridone (5a) as isolated product, but the yield was improved from 14 to 36%. The dihydrothiazole (1b), however, gave a new labile product isolated by chromatography which has been assigned the valence isomeric structure (7b); 6-methyl-2-thia-5-azatricyclo[4.3.0.0^{1,5}]non-7-en-9-one on the basis of spectroscopic data; very little of the pyridone (2b) was seen (t.l.c.). The ^{1}H n.m.r. spectra had 3- and 4-H as multiplets at *ca.* δ 3.0 and 3.5 due to geminal and vicinal couplings. H-7 resonated as a doublet at δ 7.35 and H-8 at 5.92 ($J_{7,8}$ 6 Hz). These shifts agree well with the values δ 7.65 and 5.93 given for the corresponding protons in 6-phenyl-6-azabicyclo[3.1.0]hex-3-en-2-one where the coupling between the vinylic protons also was 6 Hz. The CO absorption in the i.r. of the latter was reported as 1 725 cm^{-1},[2] which compares well with 1 720 cm^{-1} for (7b), the values being in the range for absorption of an $\alpha\beta$-unsaturated ketone in a five-membered ring. Due to slow decomposition during the recording of ^{13}C n.m.r. spectra and the weak signals from the quaternary carbons C-1 and -6 resonances for these are not given; the values for the other carbon atoms were δ 40.1 (C-3), 53.0 (C-4), 161.7 (C-7), 132.5 (C-8), and 198.6 p.p.m. (C-9). There is a good agreement of the values for C-7, -8, and -9 with the corresponding chemical shifts δ 165.1, 133.8, and 208.0 p.p.m. for C-3, -2, and -1 in cyclopentenone, respectively.[15]

In order to attempt the conversion of the valence isomer (7b) to the pyridinone (2b) a solution of (7b) in ethyl acetate was irradiated with the medium pressure Hanovia Hg lamp. This furnished (2b) besides polymeric products and lends support to the postulate that the valence isomer (7b) is an intermediate in the photochemical rearrangement of (1b) to (2b).

Ionisation potentials ($\pm$0.05eV)

Compound	Potential (eV)
(1a)	7.12
(1b)	6.95
(2a)	7.91
(2b)	7.69
(4a)	7.12
(4b)	6.84
(5a)	7.44
(5b)	7.32
(7b)	7.93

The isomer pairs (1) : (2) and (4) : (5) as well as (7b) have been subjected to comparative mass spectrometry studies as part of our program for structure analysis of isomers in the gas phase in the mass spectrometer by measurements of ionisation potentials (IP).[16] The mass spectra of the betaines (1) and (4) have previously been

reported.[17,18] The fragmentation patterns are very similar to those of the respective pyridones (2) and (5); minor differences exist in the relative intensities. The fragmentation of the valence isomer (7b) is also closely similar to the fragmentation of its isomers (1b) and (2b) and differs marginally in relative intensities. Major fragments are due to (M — H), (M — CO), (M — CHO). (M — CO — C_2H_4), and (M — CO — C_2H_4 — CH_3CN). The IP values for the isomers, however, differ significantly (Table) which makes it possible to differentiate between the structural isomers in the gas phase. In accordance with previous findings the partial charge separation in betaines results in lower IP values than the values for their non-charged isomers.[16] The IP value for the valence isomer (7b) is *ca.* 1 eV higher than for its isomeric betaine (1b) and *ca.* 0.3 eV higher than for its isomeric pyridone (2b).

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained with a 60 or 100 MHz spectrophotometer. ^{13}C N.m.r. spectra were recorded with a JEOL FX 60 Fourier transform spectrophotometer with and without proton noise decoupling. Tetramethylsilane was the reference.

The IP values were obtained by the semilog-plot interpretation of the ionisation efficiency curves obtained with an A.E.I. MS-902 mass spectrometer as previously described.[19] The values are the average of three determinations, the deviation being ±0.05 eV. The fragmentations were recorded at 70 eV.

Formation of 5-Thiazolo- and 5-Dihydrothiazolo-[3,2-a]*-pyridinones* (2) *and* (5) *by Photolysis.*—The betaine (1.0 g) was dissolved or suspended in boiling ethyl acetate (800 ml), and the reaction mixture irradiated with a medium pressure Hanovia Hg lamp using a Pyrex filter. The progress of the reaction was monitored by t.l.c. on silica gel with EtOAc–benzene (1 : 1) as eluant. The starting material was consumed after 2—4 h. The reddish-brown mixture was then evaporated. The residual material was largely polymeric, but according to t.l.c. also contained three or four more defined products. The major component was isolated by thick layer chromatography on silica gel (Merck PF 254). The developer was EtOAc–benzene (1 : 1).

Dihydrothiazolo[3,2-a]*pyridin-5-one* (2a).[6] The yield was in the range 2—5%. Complimentary physical data:[6] δ_C ($CDCl_3$) 28.2 (C-2), 50.8 (C-3), 162.4 (C-5), 114.8 (C-6), 139.9 (C-7), 100.3 (C-8), and 147.9 p.p.m. (C-8a); $\lambda_{max.}$ (EtOH) 328 (log ε 4.11) and 243 nm (3.92); ν(KBr) 1 660, 1 600, and 1 500 cm^{-1}; *m/e* 153 (100%, M^+), 152 (31), 125 (30), 124 (5), 97 (13), 71 (4), and 70 (5).

8-*Methyldihydrothiazolo*[3,2-a]*pyridin-5-one* (2b) (4%) had m.p. 35—37 °C (acetone–hexane) (Found: C, 56.95; H, 5.4. C_8H_9NOS requires C, 57.45; H, 5.4%); δ_H 2.02 (8-Me), 3.42 (2-H), 4.51 (3-H), 6.20 (6-H, $J_{6,7}$ 8.5 Hz), 7.11 (7-H); δ_C ($CDCl_3$) 28.2 (C-2), 51.3 (C-3), 161.8 (C-5), 114.9 (C-6), 142.5 (C-7), 109.0 (C-8), 145.0 (C-8a), and 17.7 p.p.m. (8-Me); $\lambda_{max.}$ (EtOH) 345sh (log ε 3.48), 334 (3.57), and 250 nm (3.45); ν(KBr) 1 660, 1 600, and 1 500 cm^{-1}; *m/e* 167 (100%, M^+), 166 (45), 139 (18), 138 (19), 111 (7), and 70 (1).

3-*Methylthiazolo*[3,2-a]*pyridin-5-one* (5a) (14%) had m.p. 100—102 °C (acetone–hexane). When the photolysis was done using the Rayonet reactor (RPQ-100) operating at 350 nm under the conditions described below for (7b), the yield was raised to 36%. The product was isolated by thick layer chromatography (Found: C, 57.9; H, 4.1. C_7H_5NOS requires C, 58.15; H, 4.25%); δ_H 2.88 (3-Me), 6.33 (2-H, $J_{2,Me}$ 1 Hz), 6.21 (6-H, $J_{6,7}$ 7.5 Hz), 7.32 (7-H), 6.51 (8-H, $J_{7,8}$ 8.5, $J_{6,8}$ 1 Hz); δ_C ($CDCl_3$) 106.0 (C-2), 139.0 (C-3), 163.2 (C-5), 110.9 (C-6), 137.4 (C-7), 99.7 (C-8), 150.1 (C-8a), and 18.7 p.p.m. (3-Me); $\lambda_{max.}$ (EtOH) 382 (log ε 4.08), 364 (4.09), 277sh (3.60), 268 (3.72), and 235 nm (3.89); ν(KBr) 1 660, 1 600, and 1 500 cm^{-1}; *m/e* 165 (100%, M^+), 164 (2), 137 (85), 136 (12), 97 (3), 71 (32), and 70 (7).

3,8-*Dimethylthiazolo*[3,2-a]*pyridin-5-one* (5b) (7%) had m.p. 110—111 °C (acetone–hexane) (Found: C, 60.6; H, 5.0. C_8H_7NOS requires C, 60.3; H, 5.05%); δ_H ($CDCl_3$) 2.86 (3-Me), 2.15 (8-Me), 6.32 (2-H, $J_{2,Me}$ 1 Hz), 6.21 (6-H, $J_{6,7}$ 8.5 Hz), and 7.17 (7-H); δ_C ($CDCl_4$) 106.1 (C-2), 140.0 (C-3), 162.7 (C-5), 111.2 (C-6), 139.1 (C-7), 107.8 (C-8), 147.5 (C-8a), 18.8 (3-Me), and 17.5 p.p.m. (8-Me); $\lambda_{max.}$ (EtOH) 383 (log ε 3.93), 370 (3.94), 272 (3.55), and 234 nm (3.83); ν(KBr) 1 660, 1 600, and 1 500 cm^{-1}; *m/e* 179 (45%, M^+), 178 (3), 151 (42), 150 (100), 71 (16), and 70 (2).

3-*Methylthiazolo*[3,2-a]*pyridin-5-one* (5a). 3-Methylthiazolo[3,2-*a*]pyridinium perchlorate (0.80 g, 3.2 mmol) was dissolved in water (50 ml) and the pH brought to *ca.* 7. To this solution at 0 °C were added dropwise at the same time aqueous solutions of potassium hexacyanoferrate(III) (2.60 g, 8 mmol, 30 ml) and potassium hydroxide (0.85 g, 15 mmol, 20 ml). When the addition was completed, the mixture was allowed to reach room temperature (2 h). After stirring for 3 h at room temperature the mixture was neutralised with HCl and extracted with chloroform (4 × 30 ml). The chloroform solution was concentrated and subjected to thick layer chromatography as above. The title compound (63 mg, 12%) had physical data as above.

6-*Methyl*-2-*thia*-5-*azatricyclo*[4.3.0.0^{1,5}]*non*-7-*en*-9-*one* (7b). 5-Methyldihydrothiazolo[3,2-*a*]pyridinium-8-olate (0.5 g) dissolved in EtOH–EtOAc (400 ml, 1 : 1) was irradiated for 24 h at 25—35 °C using a Rayonet reactor (RPQ-100) operating at 350 nm. The R_F value was *ca.* 0.2 for the title compound on silica gel with developments by EtOAc–benzene (1 : 1). Little of pyridone (2b) (R_F *ca.* 0.1) was seen. The solution was then evaporated, the residue dissolved in a little chloroform, and chromatographed on thick layer (1.75 mm) silica gel (Merck PF 254) plates (2; 20 × 20 cm) using EtOAc–benzene (1 : 1). The band with the desired product was removed and extracted with methanol. The solution was evaporated and the residue dissolved in chloroform to remove silica which was dissolved in the methanol; methanol was used for extraction since the compound was difficult to elute from silica gel with chloroform. The chloroform solution was rechromatographed twice as above. The compound was unstable in that part of it remained as polymeric material at the point of application on the plates for each chromatographic run. Evaporation of the chloroform solution after the final chromatographic separation gave a pale yellowish oil (30 mg, 6%). Because the compound appeared to decompose slowly on storage, it was not submitted to elemental analysis, δ_H ($CDCl_3$) *ca.* 3.0 (2 H, m, 3-H_2), *ca.* 3.5 (2 H, m, 4-H_2), 1.53 (3 H, s, 6-Me), 7.35 ($J_{7,8}$ 6 Hz, 7-H), and 5.92 (8-H); δ_C ($CDCl_3$) 40.1 (C-3), 53.0 (C-4), 161.7 (C-7), 132.5 (C-8), 198.6 (C-9), and 8.4 p.p.m. (6-Me) (due to slow decomposition during the recording, the weak signals from the quaternary carbons C-6 and -1 were not identified; ν($CHCl_3$)

1 720 cm^{-1} (C=C–C=O); *m/e* 167 (100%, M^+), 166 (38), 139 (24), 138 (19), 134 (7), 113 (9), 111 (8), and 70 (21).

Formation of 8-*methyldihydrothiazolo*[3,2-a]*pyridin*-5-*one* (2b) *by irradiation of* (7b). The valence isomer (7b) (20 mg) in EtOAc (500 ml) solution at 80 °C was irradiated with a medium pressure Hanovia Hg lamp for 3 h. The solution was then evaporated and the residue separated by thick layer chromatography as above. Most of the material appeared to be polymeric (R_F 0). The band with R_F *ca.* 0.1 was scraped off, and the material eluted from the silica gel with methanol (5 mg) was identified (t.l.c., spectroscopy) as the pyridone (2b).

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REFERENCES

[1] Part 51. T. Laerum, G. A. Ulsaker, and K. Undheim, *Acta Chem. Scand.*, in the press.
[2] N. Dennis, A. R. Katritzky, and H. Wilde, *J.C.S. Perkin I*, 1976, 2338.
[3] T. Laerum and K. Undheim, *Acta Chem. Scand.*, 1978, **B32**, 68.
[4] Y. Takeuchi and N. Dennis, *Org. Magnetic Resonance*, 1975, **7**, 244.
[5] P. Groth, *Acta Chem. Scand.*, 1977, **B31**. 340.
[6] P. O. Ranger, G. A. Ulsaker, and K. Undheim, *Acta Chem. Scand.*, 1978, **B32**. 70.
[7] R. Faure, J.-P. Gally, E.-J. Vincent, and J. Elguero. *Canad. J. Chem.*, 1978, **56**, 46.
[8] P. E. Hansen and K. Undheim, *J.C.S. Perkin I*, 1975, 305.
[9] J. W. Lown and K. Matsumoto, *Canad. J. Chem.*, 1975, **49**, 3443.
[10] E. F. Ullman, *J Amer. Chem. Soc.*, 1963, **85**, 3529.
[11] J. M. Dunston and P. Yates, *Tetrahedron Letters.*, 1964, 505.
[12] K. Undheim and B. P. Nilsen, *Acta Chem. Scand.*, 1975, **B29**, 503.
[13] J. A. Barltrop, A. C. Day, and C. J. Samuel, *J.C.S. Chem. Comm.*, 1977, 598.
[14] N. Ishibe and J. Masui, *J. Amer. Chem. Soc.*, 1974 **96**. 1152.
[15] D. H. Marr and J. B. Stothers, *Canad. J. Chem.*, 1964, **42**, 1563.
[16] See for instance P.E. Hansen and K. Undheim, *Acta Chem. Scand.*, 1975, **B29**, 221, and references therein.
[17] K. Undheim and T. Hurum, *Acta Chem. Scand.*, 1972, **26**, 2385.
[18] K. R. Reistad and K. Undheim, *Acta Chem. Scand.*, 1971, **25**, 2954.
[19] G. Hvistendahl and K. Undheim, *Org. Mass. Spectrometry*, 1972, **6**, 217.