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Photoinduced Ring Transformation of Pyrido-[1,2-b]pyridazinium-4-olate

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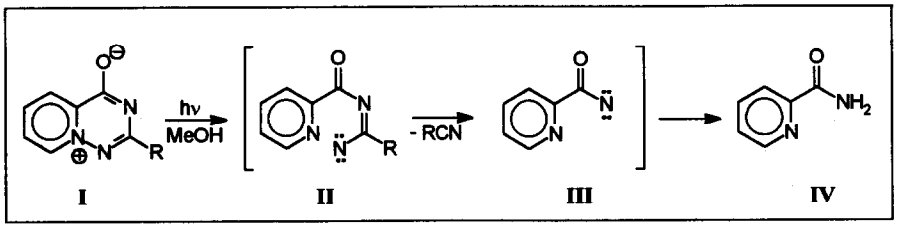
Abstract: The photolytic behaviour of the zwitterionic pyrido[1,2-*b*]pyridazinium-4-olate (**1**) was studied. A marked difference was observed depending on the wavelength used: irradiation with a light of $\lambda>280$ nm resulted in 3-phenyl-5-(2-pyridyl)isoxazole (**2**) and 2-phenyl-3-(2-pyridylcarbonyl)azirine (**3**) as main products, while the use of light of $\lambda<280$ afforded 2-phenyl-5-(2-pyridyl)-oxazole (**5**) and 1-amino-1-phenyl-3-(2-pyridyl)prop-1-en-3-one (**6**) as main products. A mechanistic suggestion is provided.

We have recently published[1] the photochemical fragmentation of pyrido[2,1-*f*]-*as*-triazinium-4-olates (**I**, R=H, C_6H_5) in methanol. It had been found that these olates (**I**), when irradiated, gave RCN and picolinic acid amide (**IV**) in good yields presumably *via* nitrene intermediates (**II** and **III**; see Scheme 1). In spite of numerous attempts, these nitrenes could be neither detected nor trapped.

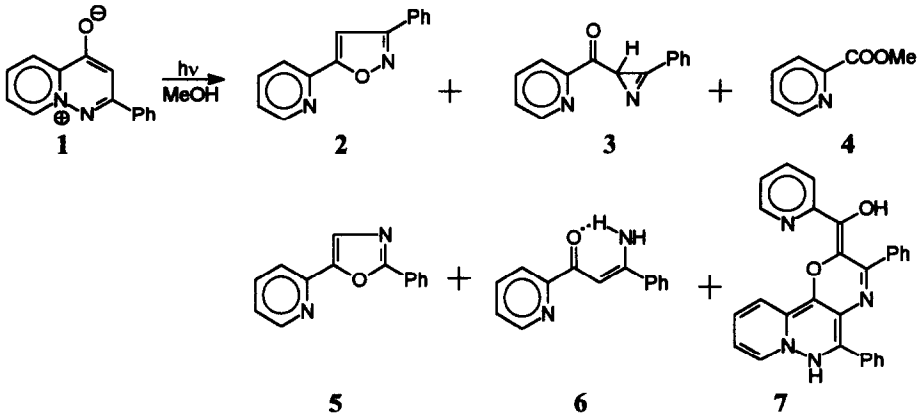


Scheme 1

In order to establish the scope and limitations of this photoreaction and to prove the validity of the proposed mechanism we now examined the photochemical behaviour of the zwitterionic system pyrido-[1,2-*b*]pyridazinium-4-olate (**1**) (containing one nitrogen less than the olate derivative **I**). The synthesis of this olate was published recently.[2]

Results:

Surprisingly, the photochemistry of olate **1** was found to display a remarkable dependence on the wavelength of the exciting light. Irradiation of **1** in methanol with a 500 W high-pressure mercury lamp gave a mixture of products **2-7**, the relative yields of which depended on the conditions applied.



Product	2	3	4	5	6	7
λ>280 nm	18 %	11 %	5 %	<1%	1.5 %	6 %
λ<280 nm	<1 %	traces	ND	36 %	14 %	1 %

ND = not detected

Scheme 2

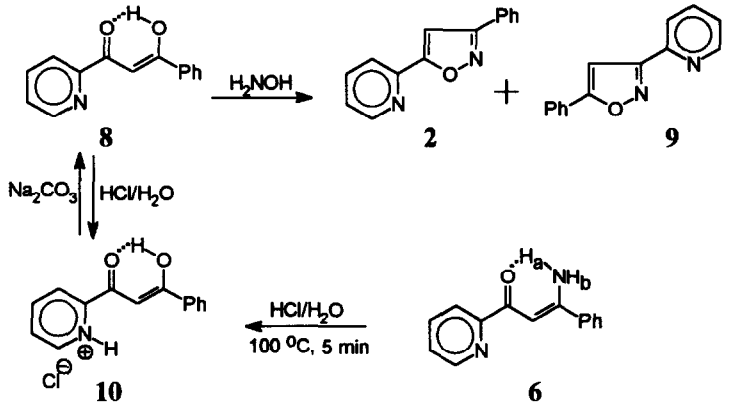
Thus, the complex product mixture obtained after irradiation of **1** for 20 hours through an immersion well made of Duran glass afforded 18 % of 3-phenyl-5-(2-pyridyl)isoxazole (**2**) as main product and 11 % of 2-phenyl-3-(2-pyridylcarbonyl)azirine (**3**) as minor component (47 % of starting material **1** was recovered). Further products were methyl 2-picolinate (**4**, 5 %), the *β*-amino-vinyl ketone **6** (1.5 %) and 3,5-diphenyl-2-[hydroxy-(2-pyridyl)]methylene-2,6-dihydro-pyrido[1',2':2,3]pyridazino[4,5-*b*][1,4]oxazine (**7**, 6 %). Less then 1 % of 2-phenyl-5-(2-pyridyl)oxazole (**5**) was additionally isolated.

When the same lamp was used in connection with quartz equipment for 21 hours, only 20 % of starting material (**1**) was recovered. The main product in this case was 2-phenyl-5-(2-pyridyl)oxazole (**5**, 36 %) and - compared to the previous experiment - an increased amount of *β*-aminovinyl ketone **6** (14 %) was isolated. The yield of oxazine derivative **7** was only 1 %, and less than 1 % of isoxazole (**2**) was obtained. Traces of azirine **3** were found in the ^{1}H-NMR spectrum of isolated **2**. Picolinic ester **4** could not be detected at all.

Structure elucidation and rationale:

The isoxazole derivative **2** was found to be identical with an authentic sample of this material prepared by a known procedure[3]: The reaction of 1-phenyl-3-(2-pyridyl)-1,3-propanedione[4] (**8**) with hydroxylamine afforded **2** together with the positionally isomeric isoxazole **9** which could be separated by chromatography.

Spectral data of compound **6** are consistent with the *cis* structure of *β*-aminovinyl ketone[5]: the NH_a proton in the intramolecular H-bridge absorbed at 3300 cm^{-1} (a similar value, 3312 cm^{-1}, was found for methyl *cis*-aminoacrylate[6]) while H_b absorbed at 3150 cm^{-1}. The ^{1}H-NMR spectrum ($CDCl_3$) of **6** also supports the chelated *cis* structure: δ H_a=10.5 ppm; H_b=5.67 ppm. Compound **6** can easily be hydrolyzed by aqueous hydrochloric acid to give the same HCl salt (**10**) which was obtained from **8**. Compound **10** may be deprotonated to give **8**.



8 **2** **9**

10 **6**

Scheme 3

The 3-picolinoyl-2-phenylazirine (**3**) displayed absorption maxima in IR spectrum (KBr) at 1770 (C=N) and 1680 (C=O) cm^{-1} (the related derivative 3-benzoyl-2-phenyl-1-azirine[7] displayed maxima at 1776 and 1669 cm^{-1}).

The ^{1}H-NMR spectrum of methyl 2-picolinate (**4**) isolated from the reaction mixture was identical with the spectrum recorded from an authentic sample.

The IR spectrum as well as the ^{1}H- and ^{13}C-NMR spectra of product **5** are characteristic for an oxazole derivative (see experimental section).

It is known that pyridazinium-4-olates[8] or pyrido[1,2-*b*]pyridazinium-4-olates containing a partially saturated pyridine ring[9,10] undergo photoisomerization to give pyrimidinone derivatives. Similarly, *s*-triazolo[4,3-*b*]pyridazinium-8-olate, when irradiated in methanolic solution gave methyl (*s*-triazolyl)amino-acrylate by rearrangement.[11]

We did not observe the formation of either aminoacrylate **11** or pyrido[1,2-*a*]pyrimidinone **12** when pyrido[1,2-*b*]pyridazinium-4-olate **1** (which contains a fully aromatic pyridine ring) was irradiated in methanolic solution. On this basis and on the basis of the isolated products we can rationalize the photolysis of **1** as follows (Scheme 4).

The scission of N-N bond of olate **1** by electronic excitation (no wavelength-dependence!) afforded of vinyl nitrene **13** similarly to **II** and according to earlier finding[1]. This highly reactive intermediate can react further in different ways:

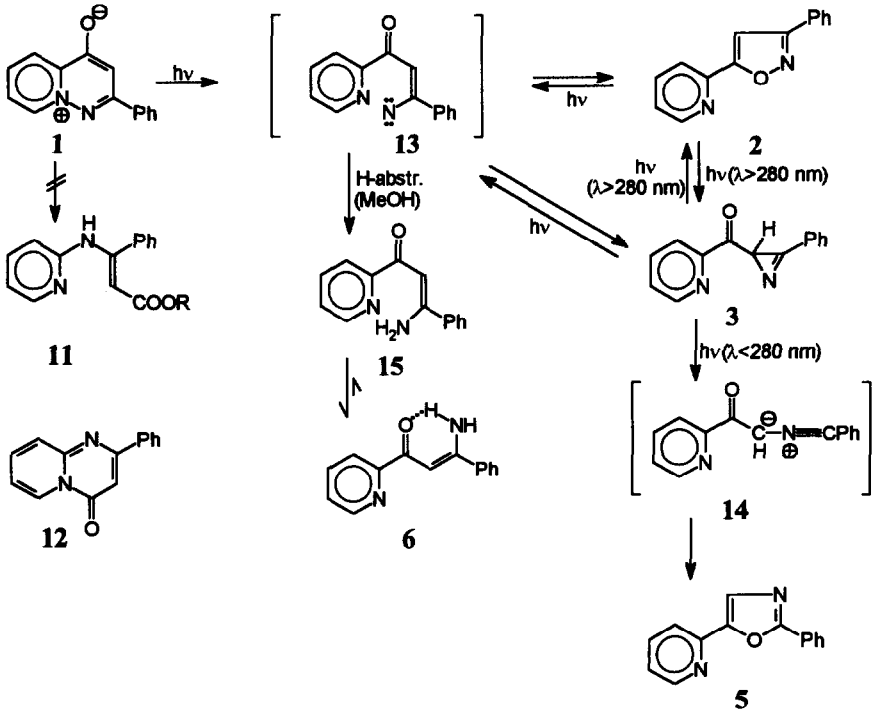
A. Cyclization to give isoxazole **2**

B. Cyclization to give azirine **3**

C. H-atom abstraction to afford **6**

D. Dimerization to form **7**

The proposed rearrangement leading to **2** and **3** (and subsequently to **5**) [**isoxazole** (⇌ vinyl nitrene) ⇌ **azirine** (⇌ nitrile ylide) ⇌ **oxazole**] is well known in the literature. Ullman and Singh[7,12] reported the wavelength-dependent photochemistry of 3,5-diarylisoxazoles. They found that 3,5-diphenyl-isoxazole gave, when irradiated with light of wavelength 254 nm, 2,5-diphenyloxazole and 3-benzoyl-2-phenyl-1-azirine. However a sharp difference was observed when this latter product was irradiated: with the light of wavelength 334 nm the only product was 3,5-diphenylisoxazole, while with light of wavelength ≤ 313 nm the only product was 2,5-diphenyloxazole.

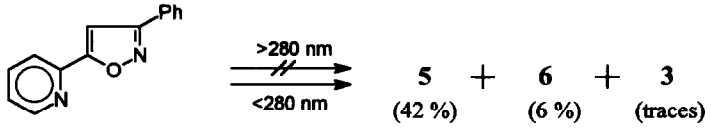


Scheme 4

They postulated in this process two "high-energy ground-state intermediates" like vinyl nitrene **13** and nitrile ylide **14** in our case. Other authors[13a-i] have supported this concept. Some review articles[14a-c] are also available on this topic.

Our findings are in good agreement with these observations: on irradiation with light of longer wavelength (>280 nm, Duran glass immersion well) isoxazole (**2**) and azirine (**3**) were formed while with light of shorter wavelength (<280 nm, quartz equipment) oxazole (**5**) was produced presumably *via* the formation of nitrile ylide intermediate (**14**).

In a separate experiment we irradiated 3-phenyl-5-(2-pyridyl)isoxazole (**2**) using different wavelength ranges.

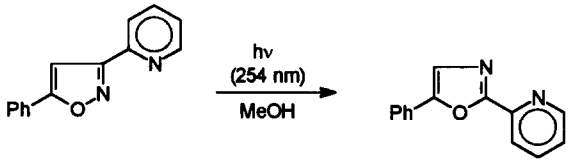


2

Scheme 5

No significant reaction occured during the irradiation of **2** through Duran glass equipment for 28 hours: starting material **2** was recovered in 82 % yield. On the other hand, irradiation with the same high-pressure mercury lamp through quartz equipment (or irradiation at 254 nm) led to a rapid rearrangement of **2** (within 4 hours) and oxazole **5** was isolated in 42 % yield together with **6** (6 %). Traces of **3** could be detected by ^{1}H-NMR.

The isomeric isoxazole (**9**) showed a similar photochemical behaviour. Its irradiation with 254 nm light afforded 5-phenyl-2-(2-pyridyl)oxazole (**16**) in 53 % yield; also the appropriate isomer of β-aminovinyl ketone **6** was detected. Compound **16** had been prepared earlier by Ott *et al.*[15] by a different (not photochemical) method.



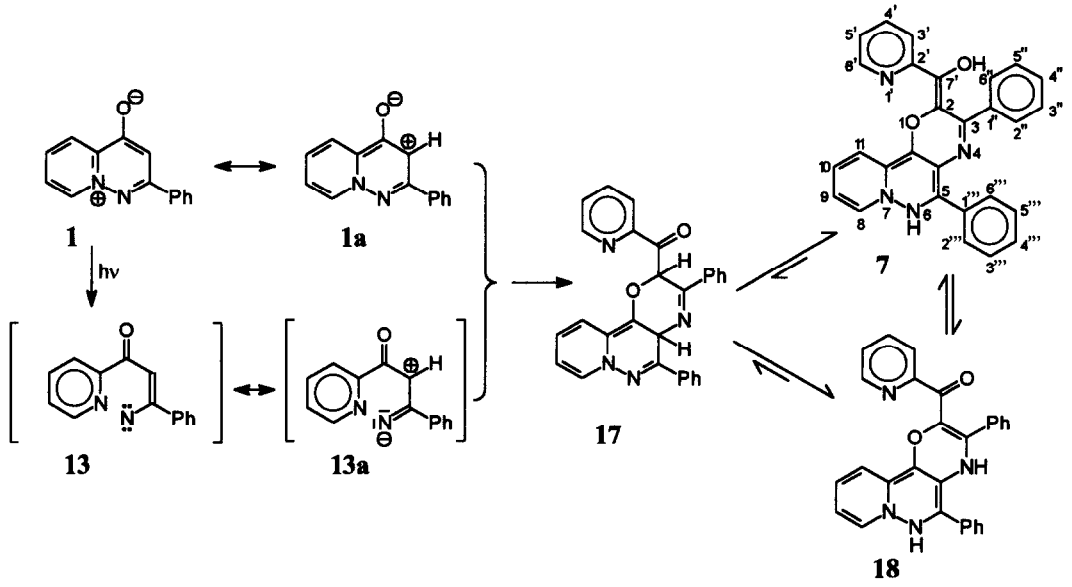
9 **16**

Scheme 6

The reactive vinyl nitrene intermediate (**13**) can react further by H-abstraction from the solvent (MeOH) to form a *β*-aminovinyl ketone (**15**) which is stabilized by a strong intramolecular H-bridge (**6**). The formation of **6** provides also a further support to the earlier proposed mechanism[1] for the photolytic fragmentation of pyrido[2,1-*f*]-*as*-triazinium-4-olate (see intermediates **II** and **III** in Scheme 1).

A further reaction pathway of nitrene **13** is its reaction with a starting olate molecule (cyclization of 1,3-dipoles; see resonance structures **1a** and **13a** in Scheme 7) to give the first representative of the new ring system: pyrido[1',2':2,3]pyridazino[4,5-*b*][1,4]-oxazine. The primary product (**17**) of the cycloaddition tautomerizes to give derivative **7** (or **18**). The structure of tautomers (**7** or **18**) was assigned by spectroscopic methods (see Experimental Section). The main fragment in the MS spectrum are: pyridine (m/e 78, 97.6 %), benzonitrile (m/e 103, 100 %), and (probably) 1-(2-pyridylcarbonyl)-2-phenylacetylene (m/e 235, 38.0 %). The retro-cycloaddition has low probability because the fragment peak 222 has even smaller intensity (8.2 %) than M^+ (444, 10.4 %). The IR spectrum in KBr does not contain any C=O band, indicating that structure **7** is the

dominant form in solid state. In $CHCl_3$ solution, however, a new band appears at 1597 cm^{-1} (of medium intensity), which can be a sign for the formation of tautomer **18** in solution.



Scheme 7

The H- and C-atoms were assigned by homo- and heterocorrelated ^1H- and ^{13}C-NMR spectra. No sp^3-type C-atom was found in the ^{13}C-NMR spectrum which excludes the tautomeric structure **17**. One of the coupling constants of α-H of the two different pyridine rings was 4.8 Hz (H-6'), indicating a "regular" 2-substituted pyridine moiety while the other, 6.8 Hz (H-8), showed the condensed structure of the other pyridine ring. The steric vicinity of the two phenyl groups was supported by the fact that NOE effect was found between their *ortho* protons (H-2", 6" *vs* H-2"', 6"'). The chemical shift of 192.95 ppm (quaternary C-atom) is indicative of a C=O group, supporting the probable existence of tautomer **18** in $CDCl_3$ solution.

Conclusion:

To the best of our knowledge, our findings represent the first example of the photochemical rearrangement of pyridazinium-olates in which diaziridine-type intermediates are not involved. By isolation of **6** we supported our earlier observations[1] that N-N bond scission can be the primary process in photolysis of some pyridinium-fused olate systems leading to formation of reactive nitrene intermediates. The main difference between the two similar nitrenes (**II** and **13**) is that the former - posessing also an amidine-like structure - can rapidly eliminate a neutral RCN fragment to give **III** (and then **IV**), while the latter (**13**) - having a probable longer life-time - could either abstract H-atoms to give the isolated **6**, or show nitrene-typical rearrangements.

EXPERIMENTAL SECTION

Melting points were measured on a Kofler microscope. IR spectra were recorded with a Perkin Elmer 283 spectrometer, and NMR spectra with Bruker WM 300 and WP 80 spectrometers (TMS as internal standard). Mass spectra were determined on a MAT 311 A spectrometer using a standard ionising potential of 70 eV.

Light sources: A Hanau 500 W medium-pressure mercury lamp was used for most preparative experiments. For other experiments Hanau 150 W high-pressure and Hanau 15 W low-pressure mercury lamp as well a 400 W low-pressure mercury lamp reactor designed by A. Gräntzel, Karlsruhe, Germany, were used. Solutions were stirred magnetically during irradiation. All irradiations were performed under an argon atmosphere.

Irradiation (λ≥280 nm) of pyrido[1,2-*b*]pyridazinium-4-olate (1)

A solution of 2.2 g (10 mmol) of **1** in 220 ml of methanol was continuously purged with argon and irradiated with a 500 W medium-pressure mercury lamp through a water cooled immersion jacket made of Duran glass for 20 hours. The reaction mixture was filtered, concentrated and the residue was chromatographed on silica gel. A rough separation was achieved by "dry-column" flash chromatography[16] (elution first with chloroform then with chloroform/methanol (9:1 v/v)). The final purification was made by preparative layer chromatography using different solvent mixtures.

3-Phenyl-5-(2-pyridyl)isoxazole (2) (eluent: n-hexane/ethyl acetate=9:1); ~210 mg (~18 %) of colourless prisms, mp 79-80 °C (petrol ether), (Lit.[3] mp 79-80 °C). This compound was identical in all respects with an authentic sample of **2**.

2-Phenyl-3-(2-pyridylcarbonyl)azirine (3): (eluent: n-hexane/ethyl acetate=9:1); ~130 mg (~11 %) of pale yellow oil; Ms: m/e 222 (M^+, 98 %), 194 (24 %), 144 (100 %), 116 (50 %), 106 (15.7 %), 91 (17.3 %), 89 (23.7 %), 77 (66 %), 63 (15.9 %), 51 (46.5 %); IR (KBr): 3050, 2995, 1770, 1680, 1595, 1580, 1565, 1485, 1460, 1450, 1435, 1400, 1340, 1325, 1250, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.77 (dd, $J_{5',6}$=5.7 Hz, $J_{4',6}$=1.7 Hz, $J_{3',6'}$=0.9 Hz, 1H, H-6'), 8.07 (dd, $J_{3',4'}$=7.8 Hz, $J_{3',5'}$=1.3 Hz, $J_{3',6'}$=0.9 Hz, 1H, H-3'), 7.90 (m, 2H, H-2",6"), 7.86 (td, $J_{3',4'}$=7.8 Hz, $J_{4',5'}$=7.7 Hz, $J_{4',6'}$=1.7 Hz, 1H, H-4'), 7.65-7.45 (m, 4H, H-5',3",4",5"), 4.56 (s, 1H, H-3) ppm; ^{13}C-NMR ($CDCl_3$): δ 197.80, 156.73, 153.62, 149.09, 137.10, 136.95, 133.64, 129.19, 127.37, 122.39, 122.11, 33.02 ppm.

Methyl 2-picolinate: (4) (eluent: chloroform/methanol=95:5); ~35 mg (~5 %) of pale yellow oil; ^{1}H-NMR ($CDCl_3$): δ 8.83 (dd, $J_{5,6}$=5.0 Hz, $J_{4,6}$=1.5 Hz, 1H, H-6), 8.22 (dd, $J_{3,4}$=7.5 Hz, $J_{3,5}$=1.0 Hz, 1H, H-3), 7.91 (td, $J_{3,4}$=7.5 Hz, $J_{4,5}$=7.5 Hz, $J_{4,6}$=1.5 Hz, 1H, H-4), 7.57 (m, 1H, H-5), 4.03 (s, 3H, CH_3) ppm. This compound was identical with an authentic sample of **4**.

2-Phenyl-5-(2-pyridyl)oxazole (5): (eluent: chloroform/methanol=95:5); 10 mg (0.9 %) of pale yellow needles (cyclohexane); mp 84-85 °C; Ms: m/e 222 (M^+, 100 %), 194 (13.8 %), 166 (2.9 %), 144 (7.7 %), 119 (77.5 %), 116 (34.3 %), 91 (45.7 %), 63 (21.2 %); IR (KBr): 3040, 1670, 1605, 1575, 1530, 1480, 1470, 1435, 1425,

1125 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.63 (dd, $J_{3',6'}$=1.0 Hz, $J_{4',6'}$=1.6 Hz, $J_{5',6'}$=4.8 Hz, 1H, H-6'), 8.14 (m, 2H, H-2",6"), 7.81 (s, 1H, H-4), 7.76 (td, $J_{3',4'}$=$J_{4',5'}$=7.8 Hz, $J_{4',6'}$=1.7 Hz, 1H, H-4'), 7.71 (dd, $J_{3',4'}$=7.9 Hz, $J_{3',5'}$=1.9 Hz, $J_{3',6'}$=1.1 Hz, 1H, H-3'), 7.47 (m, 3H, H-3",4",5"), 7.21 (dd, $J_{3',5'}$=1.9 Hz, $J_{4',5'}$=7.8 Hz, $J_{5',6'}$=4.8 Hz, 1H, H-5'); ^{13}C-NMR ($CDCl_3$): δ 161.60 (C-2), 150.51 (C-5), 149.64 (C-6'), 147.03 (C-2'), 136.56 (C-4'), 130.39 (C-4"), 128.56 (C-3",5"), 126.90 (C-1"), 126.65 (C-4), 126.24 (C-2",6"), 122.53 (C-5'), 118.86 (C-3') ppm.
Anal Calcd. for $C_{14}H_{10}N_2O$: C, 75.66 %; H, 4.54 %; N, 12.61 %. Found C, 75.73 %; H, 4.59 %; N, 12.58 %.

1-Amino-1-phenyl-3-(2-pyridyl)prop-1-en-3-one: (**6**) (eluent: chloroform/methanol= 95:5); ~20 mg (1.5 %) of pale yellow oil (solidifies on longer standing); Ms: m/e 224 (M^+, 30 %), 222 (77.7 %), 196 (34.4 %), 195 (58.9 %), 146 (100 %), 119 (48.2 %), 116 (22.6 %), 105 (25.5 %), 103 (43.7 %), 91 (40.6 %), 89 (18.2 %), 71 (26.6 %), 51 (17.7 %); IR (KBr): 3300, 3150, 3040, 2995, 1600, 1570, 1550, 1525, 1485, 1460, 1390, 1335 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 10.49 (s, 1H, NH_a), 8.65 (dd, $J_{3',6'}$=0.9 Hz, $J_{4',6'}$=1.7 Hz, $J_{5',6'}$=4.7 Hz, 1H, H-6'), 8.15 (dt, $J_{3',6'}$=0.9 Hz, $J_{3',4'}$=7.8 Hz, 1H, H-3'), 7.82 (td, $J_{3',4'}$=$J_{4',5'}$=7.8 Hz, $J_{4',6'}$=1.8 Hz, 1H, H-4'), 7.70 (m, 2H, H-2",6"), 7.46 (m, 3H, H-3",4",5"), 7.36 (dd, $J_{3',5'}$=1.3 Hz, $J_{4',5'}$=7.5 Hz, $J_{5',6'}$=4.7 Hz, 1H, H-5'), 6.93 (t, J=0.9 Hz, 1H, H-2), 5.66 (s, 1H, NH_b) ppm.

2-Phenylpyrido[1,2-*b*]pyridazinium-4-olate: (**1**) (eluent: chloroform/methanol=9:1); ~1 g (~ 47 %) of starting material **1** was recovered. Mp 191-193 °C (acetonitrile), (Lit.[2] mp 193-194 °C).

3,5-Diphenyl-2-[hydroxy-(2-pyridyl)]methylene-2,6-dihydro-pyrido[1',2':2,3]pyridazino[4,5-*b*][1,4]-oxazine (**7**): (eluent: chloroform/methanol=9:1); ~70 mg (~ 6 %) of yellow crystals, mp 229-231 °C (ether-methanol); Ms: m/e 444 (M^+, 10,4 %), 415 (5.6 %), 387 (8.6 %), 351 (5.8 %), 341 (9.7 %), 323 (15.7 %), 235 (38 %), 222 (8.2 %), 207 (6.9 %), 181 (5.3 %), 132 (7 %), 106 (28.9 %), 103 (100 %), 78 (97.6 %), 51 (21.4 %), 40 (29.4 %); IR (KBr): 3270, 3100, 3056, 1590 (medium), 1562 (very strong), 1545 (medium), 1510, 1480, 1460, 1440, 1405, 1305, 1290, 1190, 1170, 1100, cm^{-1}. IR ($CHCl_3$): 3476, 3060, 1597 (medium), 1585 (medium), 1565 (very strong), 1545 (weak), 1461 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 8.58 (d, $J_{8,9}$=6.8 Hz, 1H, H-8), 8.51 (d, $J_{10,11}$=8.4 Hz, $J_{9,11}$=1.6 Hz, 1H, H-11), 8.14 (d, $J_{2',3'}$=4.7 Hz, 1H, H-6'), 7.79 (d, $J_{4',5'}$=7.9 Hz, 1H, H-3'), 7.74 (t, $J_{9,10}$=6.7 Hz, 1H, H-10), 7.66 (dt, $J_{4',5'}$=7.8 Hz, $J_{2',4'}$=1.6 Hz, 1H, H-4'), 7.48 (dt, $J_{8,9}$=6.8 Hz, $J_{9,11}$=1.7 Hz, 1H, H-9), 7.45 (d, J=7.4 Hz, 2H, H-2",6"), 7.34 (m, 1H, H-4"), 7.26 (t, J=7.7 Hz, 2H, H-3",5"), 7.15 (t, J=7.5 Hz, 1H, H-4'"), 7.09 (dd, $J_{2',3'}$=4.9 Hz, $J_{3',4'}$=7.3 Hz, 1H, H-5'), 6.97 (t, J=7.8 Hz, 2H, H-3'",5'"), 6.73 (d, J=7.5 Hz, 2H, H-2'",6'"), 5,4 (broad s, NH) ppm. ^{13}C-NMR ($CDCl_3$): δ 192.9 (C-7'), 167.4 (C-4a), 165.8 (C-5), 161.5 (C-3), 159.6 (C-2'), 146.0 (C-6'), 141.7 (C-11a), 137.7 (C-1"), 137.6 (C-1'"), 137.2 (C-8), 136.9 (C-4'), 131.5 (C-10), 129.6 (C-2",6"), 129.2 (C-4'"), 128.5 (C-4"), 127.7 (C-3'",5'"), 127.6 (C-3",5"), 127.5 (C-2'",6'"), 124.4 (C-11), 123.8 (C-5'), 123.0 (C-9), 122.6 (C-11b), 122.5 (C-3'), 100.0 (C-2) ppm.

Irradiation (unfiltered) of pyrido[1,2-*b*]pyridazinium-4-olate (1)

A solution of 2.22 g (10 mmol) of **1** in 220 ml of methanol was continuously purged with argon and irradiated with a 500 W medium-pressure mercury lamp through a water cooled quartz jacket for 21 hours. The reaction mixture was worked up as given in the previous procedure to give: 7 mg (0.4 %) of **2**; 636 mg (36.0 %)

of **5**; 250 mg (14 %) of **6**; 20 mg (1 %) of **7**, and 450 mg (20 %) of recovered **1**. Signals of traces of **3** have been found in the ^{1}H-NMR spectrum of **2**.

Irradiation (λ≥280 nm) of 3-phenyl-5-(2-pyridyl)isoxazole (2)

A solution of 0.44 g (2 mmol) of **2** in 150 ml of methanol was irradiated with a 150 W high-pressure mercury lamp through a water cooled Duran glass jacket for 28 hours. The reaction mixture was concentrated and the residue was chromatographed on silica gel to give 0.36 g (~82 %) of starting material (**2**), mp 78-80 °C.

Irradiation (using unfiltered light) of 3-phenyl-5-(2-pyridyl)isoxazole (2)

Method A

The same irradiation as above was performed through a water cooled quartz jacket for 4 hours. Work-up of the reaction mixture gave 170 mg (~39 %) of **5**, mp 83-85 °C and 45 mg (10 %) of **6**.

Method B

A solution of 0.44 g (2 mmol) of **2** in 120 ml of methanol was irradiated with a 15 W low-pressure mercury lamp through a quartz immersion jacket for 7 hours. After concentration of the reaction mixture, the residue was chromatographed on silica gel to give 20 mg (~ 4 %) of recovered **2** contaminated by traces of **3** (detected by ^{1}H-NMR); 280 mg (~ 42 %) of **5**, mp 83-85 °C and 40 mg (6 %) of **6**.

1-Phenyl-3-(2-pyridyl)-1,3-propanedione HCl salt (10)

Method A

A solution of 60 mg (0.26 mmol) of **6** in 2 ml of 20 % HCl was refluxed for 5 min. The reaction mixture was cooled, left in a refrigerator for a night and filtered off, washed with ethyl acetate and diethyl ether to give 50 mg (70 %) of yellow needles, mp 154-156 °C; IR (KBr): 3100, 3070, 2530, 2260, 1595, 1520, 1455, 1385, 1300, 1280, 1240 cm^{-1}.

The deprotonation of this HCl salt afforded **8**, identical with an authentic sample.

Method B

0.11 g (0.5 mmol) of **8** was refluxed in 4 ml of 20 % HCl for 2 min. The reaction mixture was then cooled, left in a refrigerator for a night and filtered off, washed with ethyl acetate and diethyl ether to give 115 mg (89 %) of yellow needles, mp 155-156 °C. This compound was identical with that of obtained by *Method A*.

Irradiation (254 nm) of 5-phenyl-3-(2-pyridyl)isoxazole (9)

A solution of 0.44 g (2 mmol) of **9** in 120 ml of methanol was irradiated with a 15 W low-pressure mercury lamp for 3 hours. The reaction mixture was concentrated and the residue was chromatographed on silica gel to give 235 mg (~53 %) of pale yellow crystals (**16**), mp: 95-97 °C (Lit.[15] mp 96.5-97 °C).

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