HETEROCYCLES, Vol. 65, No. 12, 2005, pp. 2861 - 2870
Received, 11th July, 2005, Accepted, 13th October, 2005, Published online, 14th October, 2005

REACTIONS OF 4-PENTENOIC ACID WITH SULFENYL CATIONS GENERATED ELECTROCHEMICALLY FROM BISQUINOLINYL AND BISPYRIDINYL DISULFIDES

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Abstract - Lactonization of 4-pentenoic acid to 5-(azinylthio)methyloxolan-2-ones (**8**) was performed by addition of electrochemically generated azinylsulfenyl cations starting from the respective 3,3'-bis(pyridinyl or quinolinyl) disulfides (**2**) or (**5**) and 4,4'-bis(7-chloroquinolinyl or 3-methylthioquinolinyl) disulfides (**6b**), (**6c**) and using a bromide ion as a redox catalyst. Sulfenyl cations generated in the same manner from 2,2'-bispyridinyl and 2,2'-bisquinolinyl disulfides (**1**) or (**4**) reacted with 4-pentenoic acid to form thiazolo[3,2-*a*]pyridinio- or quinoliniopropanoate (**9a**) or (**9b**). In the case of 8,8'-bisquinolinyl disulfide (**7**), oxolan-2-one (**8e**) was accompanied by 2,3-dihydro-1,4-thiazinequinolinio derivative (**10**). 4,4'-Bis(pyridinyl nor quinolinyl) disulfides (**3**) and (**6a**) did not give such products.

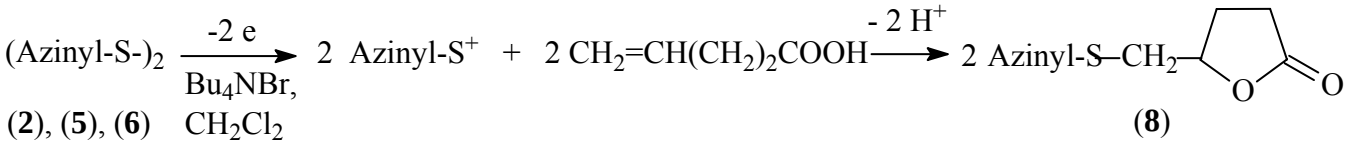
INTRODUCTION

Electrochemically generated phenylsulfenyl cation reacts with 4-pentenoic acid to form 5-(phenylthio)methyloxolan-2-one. [1] The same reaction course was observed when 3,3'-bis(4-substituted quinolinyl) disufides were used as a source of quinolinylsulfenyl cation. [2] To evaluate the scope of this reaction, we selected further diazinyl disulfides including 2,2'-, 3,3'-, 4,4'-, 4,4'-bis(3-, or 7-substituted quinolinyl)-, and 8,8'-bisquinolinyl disulfides (**4**), (**5**), (**6a**,**b**,**c**) and (**7**), as well as 2,2'-, 3,3'-, 4,4'-bispyridinyl disulfides (**1**-**3**). Our study showed that in the case of 2,2'- and 8,8'- isomers (**1**), (**4**) and (**7**) the neighbor endocyclic nitrogen atom affects the reaction course and induces the cyclization of the reaction mixture components to thiazolo- and thiazinequinolinium or pyridinium betaines (**9**) or (**10**).

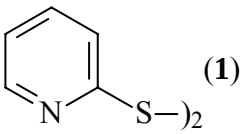
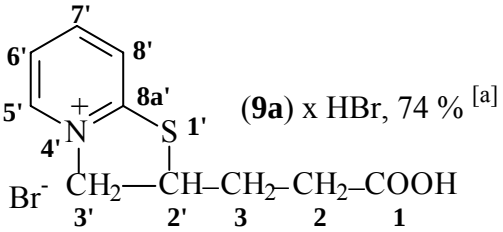
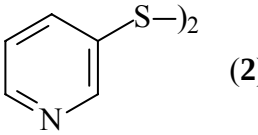
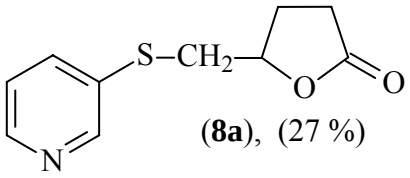
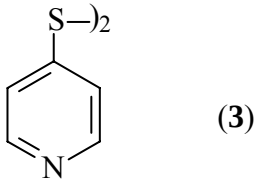
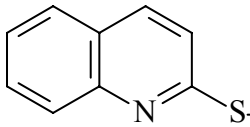
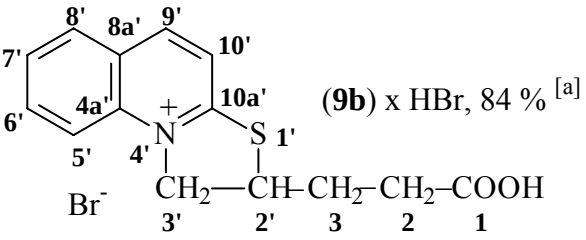
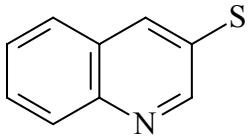
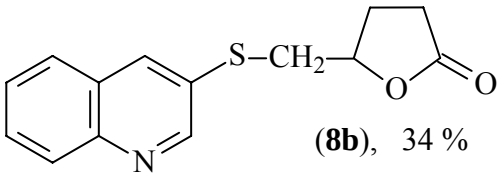
RESULTS AND DISCUSSION

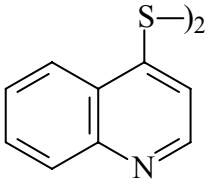
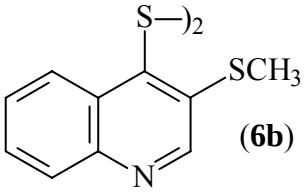
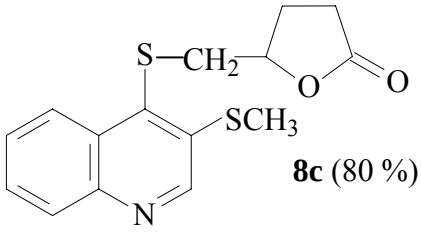
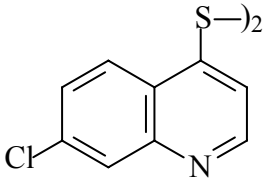
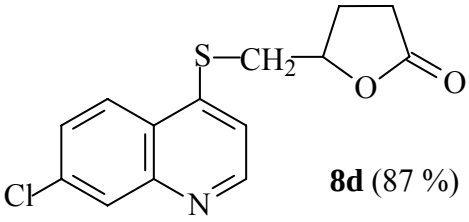
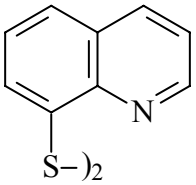
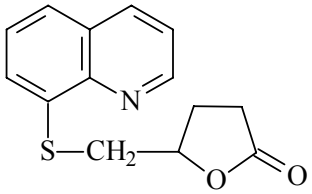
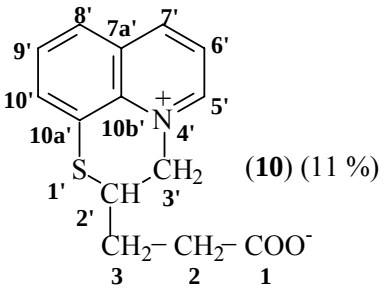
We started with the reaction of bis(γ-quinolinyl) disulfides (**6**). In the case of bis(3-methylthio) and bis(7-chloro) derivatives (**6b**) and (**6c**), the reaction of electrochemically generated sulfenyl cations with 4-pentenoic acid proceeds *via* expected pathway and gives the respective 5-(4-quinolinylthio)methyl-oxolan-2-ones (**8**) in good yields. (Table, Entries 7 and 8).

S c h e m e 1



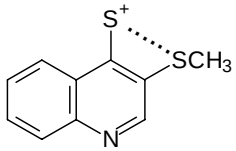
Table

Entry	Substrate	Working Potential [V]	Product
1	 (**1**)	1.25	 (**9a**) x HBr, 74 % [a]
2	 (**2**)	1.55	 (**8a**), (27 %)
3	 (**3**)	1.91	Passivation of working electrode (anode). Non-consumed substrate (**3**) (*ca.* 90 %) was recovered.
4	 (**4**)	1.80	 (**9b**) x HBr, 84 % [a]
5	 (**5**)	1.75	 (**8b**), 34 %

6	 (**6a**)	1.85	Passivation of working electrode (anode). Non-consumed substrate (**6a**), (*ca.* 90 %) was recovered.
7	 (**6b**)	1.85	 **8c** (80 %)
8	 (**6c**)	1.81	 **8d** (87 %)
9	 (**7**)	1.65	 **(8e)** (64%)  (**10**) (11 %)

[a] Crude products (**9a**) and (**9b**) contained varied (up to 0.5 mol equiv.) amounts of bromine, therefore the betaines were characterized as hydrogen bromides (**9a**) x HBr and (**9b**) x HBr.

4,4'-Bispyridinyl disulfide (**3**) nor 4,4'-bisquinolinyl disulfide (**6a**) did not give products of oxolanone type, although the oxidation potentials of compounds (**6a**) and (**6b**) are identical (see Table). Most probably, the sulfenyl cation (**64+**) formed from 3-methylthio derivative (**6b**) is stabilized by interaction with the *ortho*-methylthio group. [3]


(**64**$^+$)

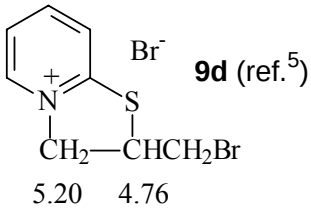
Low yields in the preparation of oxolan-2-ones (**8a**) and (**8b**) from 3,3'-bispyridinyl disulfide (**2**) and 3,3'-bisquinolinyl disulfide (**5**) may be due to the low stability of compounds (**8a**) and (**8b**) as compared to the properties of 4-substituted derivatives of **8b**. [2] All oxolan-2-ones (**8a**,**b**,**c**,**b**,**e**) showed the positive hydroxyamic test [4] for the lactone moiety.

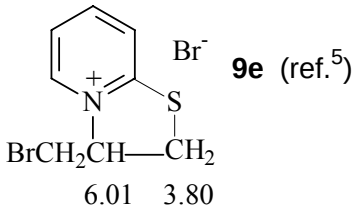
Sulfenyl cations generated electrochemically from 2,2'-bispyridinyl and 2,2'-bisquinolinyl disulfides (**1**) and (**4**) readily reacted with 4-pentenoic acid to form the products which did not contain a lactone function, and also their other properties (e.g. higher melting points, Rf values) differ from those of oxolanones (**8**). Considering the formation of the above mentioned oxolan-2-ones (**8**) in terms of

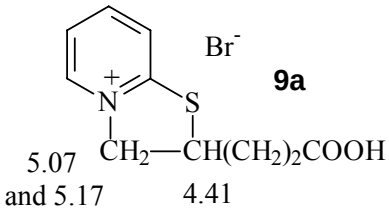
alkylation of thioazine species, literature review was performed. It revealed that the addition of bromine to 2-allylthiopyridine led either to 3-bromomethyl-2,3-dihydrothiazolo[3,2-*a*]pyridinium bromide (**9e**) (at 0-5 ºC) or to 2-bromomethyl-2,3-dihydrothiazolo[3,2-*a*]pyridinium bromide (**9d**) (at room temperature). [5] Furthermore, 2-bromo-3-(2-pyridinylthio)butyric acid underwent cyclization to 2-methyl-2,3-dihydro thiazolo[3,2-*a*]-pyridinium-3-carboxylate. [6] It suggests that the interaction of α-pyridine – or α-quinolinesulfenyl cations with pentenoic acid may lead to the formation of 2,3-dihydrothiazolo[3,2-*a*]-pyridinium species of type (**9**). Furthermore, if the sulfenylation of alkenes follows the Markovnikov rule, [1] the reactions with α,α'-diazinyl disulfides (**1**) and (**4**) should give products with *S*-CH_2 groups of type (**9c**). However, the chemical shift values δ_H of S-CH and N^+-CH_2 protons in ^{1}H NMR spectra of our products (**9a**) and (**9b**) fit well the respective data reported [5] for isomeric salt (**9d**). (Scheme 2)

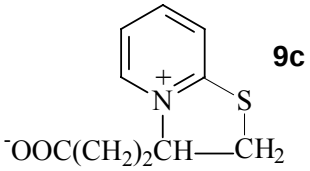
S c h e m e 2

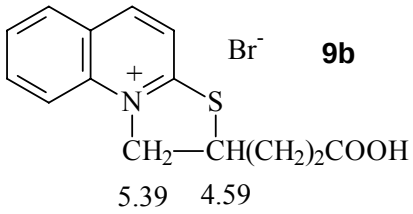
The chemical shift values δ_H [ppm] for protons from *S*- and *N*-methylene or methine groups in salts (**9**) and (**10**)

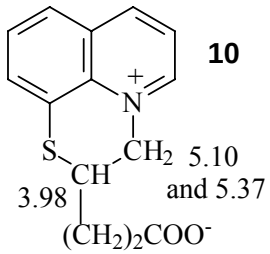










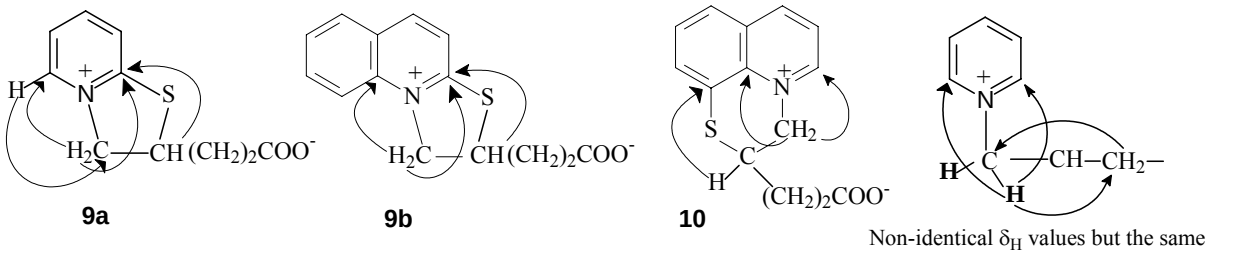


To prove this supposition a total analysis of the ^{1}H and ^{13}C NMR spectra of products (**9a**, **9b** and **10**) was performed using 1D and 2D NMR spectrometry (including HSQC and HMBC). The crucial data in the structure assignment of **9a**, **9b** and **10** come from the long-range proton-carbon correlations deduced from HMBC spectra. They show the connectivity links between *N*-methylene protons and both α-azinyl carbons as well as S-CH protons and $C_{arom.}$-S carbons. (see Scheme 3) Due to the folded shape of the dihydrothiazole and dihydrothiazine moiety in compounds (**9a**) and (**10**), respectively, two signals of C-H protons (from *N*-CH_2 groups) were observed. However, they exhibited the same one-bond and long-range proton carbon correlation. This effect was observed previously by Cox *et al*. [9]

The formation of **9a** and **9b** could be explained taking into account the well documented fact that alkenes react with sulfenyl halides *via* thiiranium intermediates. [7,8] Therefore, the primarily formed azinyl cation should interact with 4-pentenoic acid to form thiiranium species (**T**$^+$). (Scheme 4)

Scheme 3

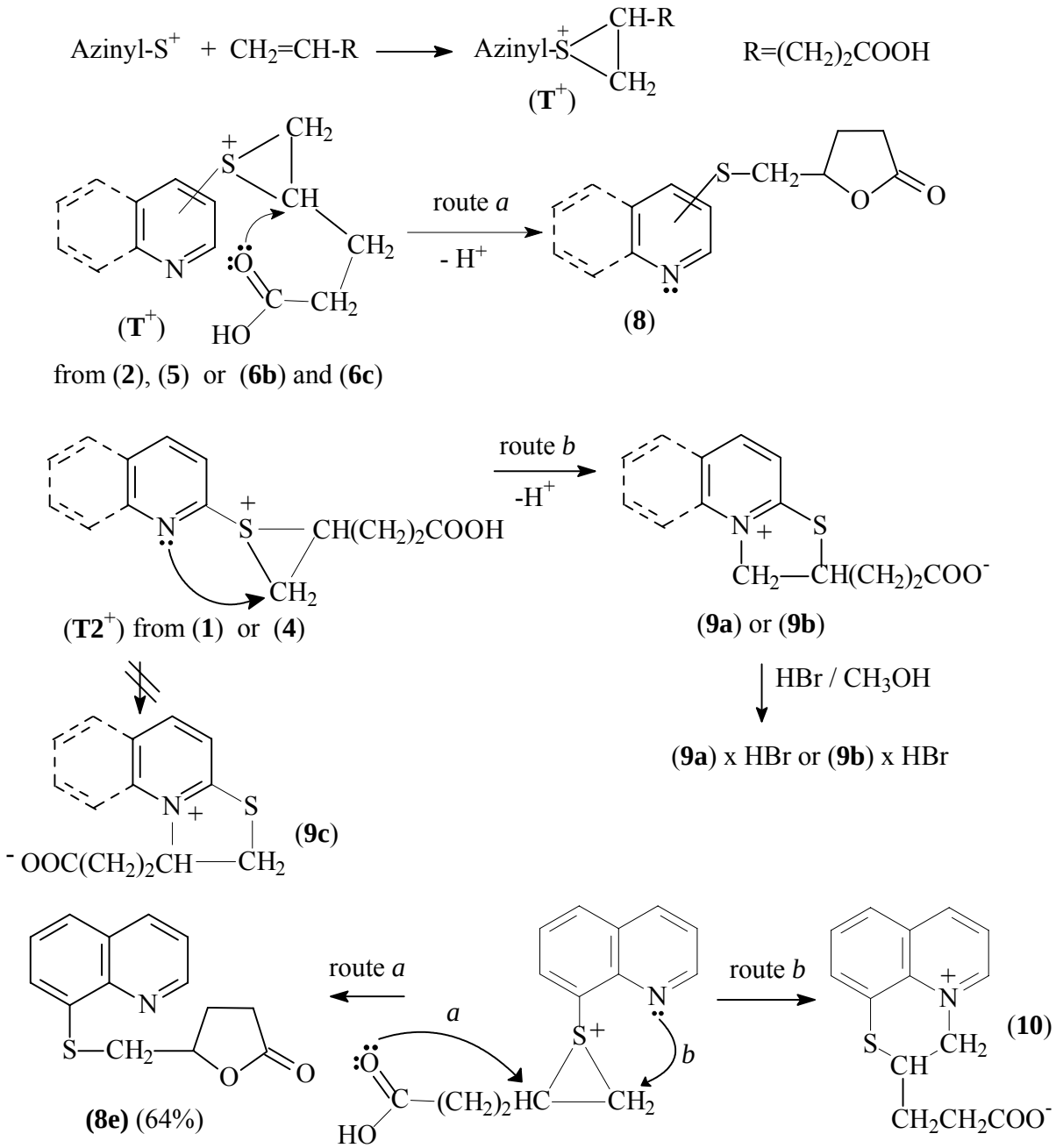
Selected three-bond proton-carbon correlations deduced from HMBC spectra of **9a** , **9b** and **10**



9a **9b** **10**

Non-identical δ_H values but the same proton-carbon correlation were observed for both bolded **H** atoms from N-CH_2 groups of betaines (**9a)** and (**10)**.

Scheme 4



These species formed from 3-pyridine and 3- or 4-quinoline derivatives (**2**, **5**, **6b**, **6c**) would rearrange to oxolanones (**8**) (Scheme 4, route *a*). However, ring enlargement of thiiranium species (**T2**$^+$) formed from α-azinylsulfenyl cations to thiazolium moiety in betaines (**9a**) or (**9b**) should start with less hindered site as nucleophilic displacement of methylene group by azine *endocyclic* nitrogen atom. Thus, as suggested by Kim [5] for the formation of **9d**, thiiranium species (**T**$^+$) formed from α-azinylsulfenyl cations underwent transformation to *anti*-Markovnikov products (**9a**) or (**9b**) containing *N*-methylene group (Scheme 4, route *b*). In the case of 8-quinolinyl isomer (**7**), the competition between the transformations of *S*-(8-quinolinyl)thiiranium salt to oxolanone (**8e**) and thiazinium betaine (**10**) was observed.

CONCLUSIONS

Two types of products, *i.e.* azinylthiooxolanones (**8**) and thiazolium betaines (**9**) or thiazinium betaine (**10**) were obtained after the electrolysis of bispyridinyl and bisquinolinyl disulfides (**1**-**7**) in the presence of 4-pentenoic acid. Their formation could be rationalized assuming the interaction of azinylsulfenyl cation with 4-pentenoic acid, which leads to the formation of azinylthiiranium species (**T**$^+$). The latter should undergo final transformation either by nucleophilic cleavage of thiirane ring with carboxylic oxygen to form oxolanones (**8**) or by *endocyclic* nitrogen to give betaines (**9**) and (**10**).

EXPERIMENTAL

All melting points are uncorrected. All NMR spectra were recorded on a Bruker AVANS 400 spectrometer operating at 400.22 MHz and 100.64 MHz for ^{1}H and ^{13}C nuclei, respectively, in deuterochloroform or in hexadeuterodimethyl sulfoxide solutions with tetramethylsilane (δ 0.0 ppm) as internal standard. Two-dimensional ^{1}H-^{13}C HSQC and HMBC experiments were performed using standard Bruker software HSQCGP and HMBCGP, respectively, and the following parameters: the spectral widths in F_2 and F_1 were *ca* 5 kHz for ^{1}H and 16.7 kHz for ^{13}C, the relaxation delay was 1.5 s, the refocusing in the HSQC experiment was 1.7 ms and the delay for long-range evolutions was 50 ms in ^{1}H / ^{13}C HMBC. 2D spectra were acquired as 2048 x 1024 hypercomplex files, with 1-4 transients. EIMS spectra were determined on a Finnigan MAT 95 spectrometer at 70 eV.

TLC analyses were performed employing Merck's silicagel 60 F_{254} plates using a mixture of methylene chloride - ethanol (10:1, v/v) as an eluent.

2,2'- and 4,4'-Bispyridinyl disulfides (**1**) and (**3**) were commercial products. 3,3'-Bispyridinyl disulfide (**2**) and 3,3'-bisquinolinyl disulfide (**5**) were prepared as described previously. [10] 4,4'-Bisquinolinyl disulfides (**6a**), (**6b**), (**6c**) were prepared by oxidation of the respective 4-quinolinethiones in alkaline milleau with potassium ferricyanide. [11] 8,8'-Bisquinolinyl disulfide (**7**) was prepared from 8-chlorosulfonylquinoline.[12]

General procedure for preparative electrolysis:

Electrolysis was carried out under controlled potential in three-compartment H-cell equipped with a platinium working electrode (area 10 cm^2), a carbon rod as counter electrode and a saturated calomel electrode as a reference. Electrodes were connected to an Atlas Sollich 9833 potentiostat in combination with Atlas DC 9933 computer program. Values of oxidation potentials (determined in 0.1 M solution of tetraethylammonium perchlorate in acetonitrile) were used as working potentials for electrolysis.

A solution of disulfide (**1**-**7**) (1 mmol) in 100 mL of 0.1 M solution of tetrabutylammonium bromide in methylene chloride was electrolyzed at working potential as shown in Table. After electric current consumption of 10^{-4} F, 4-pentenoic acid (0.2 g, 2 mmol) in 2 mL of methylene chloride was added to the reaction mixture and the electrolysis was continued up to complete consumption of the starting disulfide (as monitored by TLC).

Isolation of electrolysis products:

i) The reaction mixture after the electrolysis of disulfides (**2**), (**5**), (**6b**) and (**6c**) was evaporated up to the volume of 30 mL, washed with water (3 x 30 mL), dried with anhydrous sodium sulfate. The solvent was stripped off. The residue was purified by column chromatography on silica gel 60 (Merck) using a mixture of methylene chloride - ethanol (10:1, v/v) as an eluent. The solid samples of **8c** and **8d** were recrystallized from acetone. Oxolanones (**8a**) and (**8b**) were obtained as thick oils.

ii) In the case of disulfide (**7**) the reaction mixture was filtered off to give 0.06 g (11 %) of thiazinium betaine (**10**), which was then recrystallized from methanol containing 3 drops of 48 % aqueous hydrogen bromide to give pure hydrogen bromide of salt (**10**). The filtrate was then worked up as above to give oxolanone (**8e**).

iii) The reaction mixture after the electrolysis of disulfides (**1**) or (**4**) was filtered off to give crude thiazolium derivatives (**9a**) or (**9b**), respectively. The sample of **9a** was recrystallized from methanol to afford crystals of semi bromine complex of **9a**. The samples of crude **9a** and **9b** were recrystallized from methanol containing 3 drops of 48 % aqueous hydrogen bromide to give pure hydrogen bromides of **9a** and **9b**.

ix) In the case of disulfides (**3**) and (**6a)** the consumption of electric current has stopped within 20 min. It may be due to the passivation of the working electrode (anode) be precipitation of a thin film of polymeric material on the surface of this electrode. The electrolysis was continued for additional 2 h. The mixture was then treated as above (procedure *i*) to afford only the non-consumed starting disulfide (**3**) or (**6a)**, *ca.*90 %.

5-(3-Pyridinylthio)methyloxolan-2-one (**8a**)

An oil. EIMS (70eV) (m/z): 209 (69, M^+), 110 (100). ^{1}H NMR ($CDCl_3$), δ: 1.45-1.51 (m, 2H,

CHC$\underline{H_2}$CH$_2$), 1.67-1.73 (m, 2H, CH CH$_2$C$\underline{H_2}$), 3.33 (dd, 2H, *J*=14.0 Hz, *J*=8.0 Hz, SC$\underline{H_2}$), 4.65-4.75 (m, 1H, C$\underline{H}$O), 7.21 (dd, 1H, *J*=7.8 Hz, *J*=4.8 Hz, H5), 7.76 (ddd, 1H, *J*=7.8 Hz, *J*=2.0 Hz, *J*=1.9 Hz, H4), 8.44 (dd, 1H, *J*=4.8 Hz, *J*=1.9 Hz, H6), 8.61 (d, 1H, *J*=2.0 Hz, H2). *Anal.* Calcd for $C_{10}H_{11}NO_2S$: C 57.39; H 5.30; N 6.69. Found: C 57.12; H 5.23; N 6.47.

5-(3-Quinolinylthio)methyloxolan-2-one (**8b**)

An oil. EIMS (70eV) (m/z): 259 (82, M^+), 160 (100). ^{1}H NMR ($CDCl_3$), δ: 2.01-2.11 (m, 1H, CHC$\underline{H_2}$CH$_2$), 2.39-2.48 (m, 1H, CHC$\underline{H_2}$C$\underline{H_2}$CO), 2.50-2.67 (m, 2H, CHC$\underline{H_2}$CO), 3.19 (dd, 1H, *J*=13.9 Hz, *J*=6.9 Hz, SC$\underline{H_2}$), 3.40 (dd, 1H, *J*=13.9 Hz, *J*=5.2 Hz, SC$\underline{H_2}$), 4.64-4.71 (m, 1H, C$\underline{H}$O), 7.57 (ddd, 1H, *J*=8.1 Hz, *J*=7.0 Hz, *J*=1.1 Hz, H6), 7.71 (ddd, 1H, *J*=8.4 Hz, *J*=7.0 Hz *J*=1.4 Hz, H7), 7.77 (dd, 1H, *J*=8.1 Hz, *J*=1.4 Hz, H5), 8.08 (d, 1H, *J*=8.4 Hz, H8), 8.20 (d, 1H, *J*=2.2 Hz, H4), 8.89 (d, 1H, *J*=2.2 Hz, H2). *Anal.* Calcd for $C_{14}H_{13}NO_2S$: C 64.84; H 5.05; N 5.40. Found: 64.51; H 4.98; N 5.31.

5-(3-Methylthio-4-quinolinylthio)methyloxolan-2-one (**8c**)

mp 81-82 °C (acetone). EIMS (70 eV) m/z: 305 (100, M^+). ^{1}H NMR ($CDCl_3$), δ: 1.78-1.83 (m, 2H, CHC$\underline{H_2}$CH$_2$), 2.15-2.19 (m, 2H, CH$_2$C$\underline{H_2}$CO), 2.71 (s, 3H, SCH_3), 3.22 (d, *J*=7.3 Hz, 2H, SCH_2), 4.43-4.48 (m, 1H, CHO), 7.68-7.75 (m, 2H, 2 x H_{arom}), 8.02−8.05 (m, 1H, H_{arom}), 8.40-8.43 (m, 1H, H_{arom}), 8.86 (s, 1H, H2). *Anal.* Calcd for $C_{15}H_{15}NO_2S_2$: C 58.99; H 4.90; N 4.59; S 20.99. Found: C 58.78; H 4.80; N 4.65; S 20.23.

5-(7-Chloro-3-quinolinylthio)methyloxolan-2-one (**8d**)

mp 93-94 °C (acetone). EIMS (70 eV) m/z: 293 (37, M^+), 295 (13.5, M+2). 85 (100). ^{1}H NMR ($CDCl_3$), δ: 2.09-2.18 (m, 1H, CHC$\underline{H_2}$CH$_2$), 2.45-2.54 (m, 1H, CHC$\underline{H_2}$CH$_2$), 2.55-2.70 (m, 2H, CH$_2$C$\underline{H_2}$CO) 3.34 (dd, 1H, *J*=13.7 Hz, *J*=6.6 Hz, SCH_2), 3.52 (dd, 1H, *J*=13.7 Hz, *J*=5.4 Hz, SCH_2), 4.78-4.84 (m, 1H, C$\underline{H}$O), 7.28 (d, 1H, *J*=4.8 Hz, H3), 7.53 (dd, 1H, *J*=9.1 Hz, *J*=2.1 Hz, H6), 8.08 (d, 1H, *J*=9.1 Hz, H5), 8.09 (d, 1H, *J*=2.1 Hz, H8), 8.76 (d, 1H, *J*=4.8 Hz, H2). *Anal.* Calcd for $C_{14}H_{12}NO_2ClS$: C 57.24; H 4.12; N 4.77; S 10.92. Found: C 57.12; H 4.10; N 4.70; S 10.82.

5-(8-Quinolinylthio)methyloxolan-2-one (**8e**)

An oil. EIMS (70eV) (m/z): 259 (20, M^+), 161 (100). ^{1}H NMR ($CDCl_3$), δ: 2.45-2.65 (m, 4H, CHC$\underline{H_2}$C$\underline{H_2}$CO), 3.22-3.28 (m, 2H, SCH_2), 4.78-4.80 (m, 1H, C$\underline{H}$O), 7.49 (dd, 1H, *J*=8.0 Hz, *J*=4.4 Hz, H3), 7.50 (dd, 1H, *J*=8.0 Hz, *J*=7.0 Hz, H6), 7.64 (dd, 1H, *J*=7.0 Hz, *J*=1.2 Hz, H7), 7.67 (dd, 1H, *J*=8.0 Hz, *J*=1.2 Hz, H5), 8.18 (dd, 1H, *J*=8.0 Hz, *J*=1.6 Hz, H4), 8.98 (dd, 1H, *J*=4.4 Hz, *J*=1.6 Hz, H2). *Anal.* Calcd for $C_{14}H_{13}NO_2S$: C 64.84; H 5.05; N 5.40. Found: C 64.59; H 4.99; N 5.27.

3-(2,3-Dihydrothiazolo[3,2-*a*]pyridinio-2-yl)propanoic acid bromide (**9a**) x HBr

mp 222-224 °C (methanol). ^{1}H NMR (DMSO) δ [δ_C for carbons from single bond and / long range proton-carbon correlations]: two independent signals of H3 protons were observed: 1.99 (m, 1H) and 2.08

(m, 1H), both with the same proton-carbon correlations [28.9 (C3) / 63.9 (C3'), 173.3 (C1)], 2.40 [(m, 2H, H2); 30.8 (C2) / 46.5 (C2')], 4.41 [(quintet, 1H, *J*=7.6 Hz, *J*=7.6 Hz, *J*=7.5 Hz, *J*=4.9 Hz, H2'); 46.5 (C2') / 30.8 (C2), 158.4 (C8a')], two independent signals of H3' protons were observed: 5.07 (dd, 1H, *J*=13.6 Hz, *J*=4.9 Hz) and 5.17 (dd, 1H, *J*=13.6 Hz, *J*=7.5 Hz) both with the same proton-carbon correlations [63.9 (C3') / 28.9 (C3), 143.0 [(C5'), 158.4 (C8a')], 7.76 [(ddd, 1H, *J*=7.6 Hz, *J*=6.4 Hz, *J*=1.0 Hz, H6'); 122.6 (C6') / 123.2 (C8')], 8.16 [(dd, 1H, *J*=8.4 Hz, *J*=1.0 Hz, H8'); 123.2 (C8') / 122.6 (C6')], 8.34 [(ddd, 1H, *J*=8.4 Hz, *J*=7.6 Hz, *J*=1.0 Hz, H7'); 144.6 (C7') / 143.0 (C5'), 158.4 (C8a')], 8.92 [(dd, 1H, *J*=6.4 Hz, *J*=1.0 Hz, H5'); 143.0 (C5') / 63.9 (C3'), 144.6 (C7'), 158.4 (C8a')], 12.34 [(s, 1H, COOH) [173.3 (C1)]. *Anal.* Calcd for $C_{10}H_{12}NO_2BrS$: C 41.39; H 4.17; N 4.83. Found: C 41.34; H 4.10; N 4.62.

3-(2,3-Dihydrothiazolo[3,2-*a*]quinolinio-2-yl)propanoic acid bromide (**9b**) x HBr

mp 198-200 ºC (acetone). ^{1}H NMR (DMSO), δ: [δ_C for carbons from single bond and / long range proton-carbon correlations]: 2.16 [(m, 2H, H3); 29.7 (C3) / 60.9 (C3'), 173.4 (C1)], 2.48 [(m, 2H, H2); 30.8 (C2) / 45.6 (C2')], 4.59 (m, 1H, H2'); 45.6 (C2') / 30.8 (C2), 164.4 (C10a')], 5.39 (m, 2H, H3'); 60.9 (C3') / 29.7 (C3), 138.1 (C4a'), 164.4 (C10a')], 7.89 [(ddd, 1H, *J*=8.0 Hz, *J*=7.2 Hz, *J*=1.0 Hz H7'); 128.2 (C7') / 118.7 (C5'), 126.6 (C8a')], 8.15 [(ddd, 1H, *J*=8.0 Hz, *J*=7.2 Hz, *J*=1.2 Hz, H6'); 134.8 (C6') / 130.7 (C8'), 138.1 (C4a')], 8.19 [(d, 1H, *J*=8.9 Hz, H10'); 118.8 (C10') / 128.6 (C8a')], 8.24 [(dd, 1H, *J*=8.4 Hz, *J*=1.0 Hz, H5'); 118.7 (C5') / 126.6 (C8a'), 128.2 (C7')], 8.33 [(dd, 1H, *J*=8.0 Hz, *J*=1.2 Hz, H8'); 130.7 (C8') / 134.8 (C6'), 138.1 (C4a'), 147.3 (C9')], 8.93 [(d, 1H, *J*=8.9 Hz, H9'); 147.3 (C9') / 130.7 (C8'), 138.1 (C4a'), 164.4 (C10a')], 12.35 [(s, 1H, C1); 173.4 (C1)]. *Anal.* Calcd for $C_{14}H_{14}NO_2BrS$: C 49.42; H 4.15; N 4.12. Found: C 49.21; H 4.05; N 3.83.

3-(2,3-Dihydro-1,4-thiazine[2,3,4-*i*,*j*]quinolinio-2-yl)propanoate (**10**) [13]

mp 242-244 ºC (acetone). EIMS (70eV) (m/z): 259 (61, M^+), 174 (100). ^{1}H NMR (DMSO), δ [δ_C for carbons from single bond and / long range proton-carbon correlations]: two independent signals of H3 protons were observed: 1.77-1.84 (m, 1H) and 2.03-2.10 (m, 1H) both with the same proton-carbon correlations [26.7 (C3) / 61.6 (C3'), 173.5 (C1)], *ca.* 2.50 [(m, 2H, H2); 30.7 (C2) / 35.7 (C2')], 3.98 [(m, 1H, H2'); 35.7 (C2') / 125.8 (C10a')], 5.10 [(dd, 1H, *J*=14.3 Hz, *J*=7.4 Hz, H3'); 61.6 (C3') / 35.7 (C2'), 133.0 (C10b'), 150.4 (C5')], 5.37 [(dd, 1H, *J*=14.3 Hz, *J*=2.2 Hz, H3'); 61.6 (C3') / 26.7 (C3), 133.0 (C10b'), 150.4 (C5')], 7.90 [(dd, 1H, *J*=7.9 Hz, *J*=7.9 Hz, H9'); 129.4 (C9') / 125.8 (C10a'), 130.5 (C7a')], 8.12 [(d, 1H, *J*=7.9 Hz, H10'); 132.7 (C10') / 127.0 (C8'), 133.0 (C10b')], 8.19 [(dd, 1H, *J*=8.4 Hz, *J*=5.8 Hz, H6'); 122.3 (C6') / 130.5 (C7a'), 150.4 (C5')], 8.21 [(d, 1H, *J*=7.9 Hz, H8'); 127.0 (C8') / 132.7 (C10'), 133.0 (C10b'), 148.7 (C7')], 9.29 [(d, 1H, *J*=8.4 Hz, H7'); 148.7 (C7') / 133.0 (C10b'), 150.4 (C5')], 9.41 [(d, 1H, *J*=5.8 Hz H5'); 150.4 (C5') / 61.6 (C3'), 122.3 (C6'), 133.0 (C10b'), 148.7 (C7')], and 173.5 (C1). *Anal.* Calcd for $C_{14}H_{13}NO_2S$: C 64.84; H 5.05; N 5.40; S 12.36. Found: C 64.75; H 4.99; N 5.24.

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