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Photochemistry of Phthaloylcysteine, its Methyl Ester and C-Unprotected S-Alkyl Derivatives[1]

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Abstract: N-Phthaloyl cysteine derivatives **1a-d** were photochemically transformed by elimination, decarboxylation, and *via* electron transfer cyclization to the products **2**,**3**,**4** and **6-8**. The spin selectivities of singlet and triplet pathways were investigated in acetonitrile and acetone. The excited singlets were prone to elimination and γ-H abstractions (e.g. formation of **5**) whereas the triplets cyclized to thiazinoisoindoles. This behaviour can be correlated with the efficiencies of forward and return electron transfer steps versus homolytic hydrogen abstractions as examplified for the cysteine substrate **9**.

INTRODUCTION

The spin selectivity of singlet and triplet excited phthalimide derivatives of α-amino acids in intramolecular hydrogen abstraction reactions has been investigated in the last years by us for sulfur-substituted, hydroxylated, and aryl-substituted amino acids.[2,3] An especially interesting substrate in this context was the C-unprotected N-phthaloyl methionine which did not undergo hydrogen abstraction from the first excited singlet state, but solely electron transfer initiated cyclization from the triplet state.[2] This was our first example of an C-unprotected α-amino acid not giving the corresponding decarboxylation product during direct or sensitized photolysis.[4] A similar behaviour was found later for the 3,4-dihydroxyphenylalanine (DOPA) derivative.[3] The difference in chemoselectivity between singlet and triplet excited phthalimides was also studied in detail for a series of N-phthaloyl cysteine methyl esters.[5] These substrates could be photochemically transformed

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following two modes of activation: homolytic γ-CH cleavage or intramolecular photoinduced electron transfer (PET) leading to oxidation of the sulfur atom. The former mode is energetically feasible only for the first excited singlets, PET is energetically feasible for phthalimide singlets and triplets.[5]

The C-unprotected phthalimides of cysteine, S-alkyl cysteines, and penicillamine, whose photochemical reactions are described in this communication, were expected to show photodecarboxylation in competition with sulfur oxidation depending on their structure and on the oxidation potentials of the electron donor part of the substrates.

RESULTS AND DISCUSSION

The first example investigated was phthaloyl cysteine **1a** which gave two decarboxylation products **2a** and **3a** under all solvent conditions:

Scheme 1

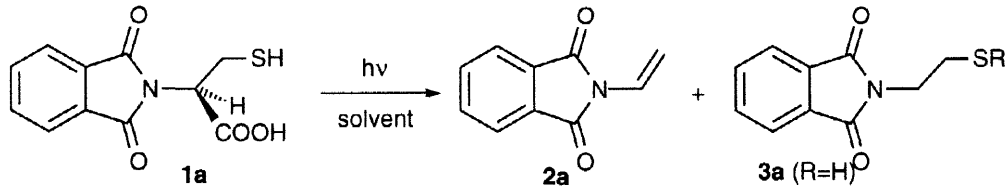


Table 1. Photolysis of **1a** - product composition[b]:

entry	solvent[a]	conversion (%)	**2a** (%)	**3a** (%)
1	acetonitrile	100	> 97	< 3
2	methanol	60	36	64
3	H_2O/acetone (50:1)	100	< 3	> 97

[a] 0.01 M solution of **1a** / pyrex / 15°C / 24 h / RPR-208 Rayonet photoreactor;
[b] ^1H NMR normalized to 100%.

The photolyses could not be performed in acetone due to the low solubility of **1a**. It was remarkable that **1a** did not give any S-oxidation products under the conditions applied (irradiation at 300 nm, r.t., N_2) despite the low oxidation potential of the thiol group (ca. 0.85 V *vs.* SCE)[6]. A reason for this phenomenon could be the rapid return electron transfer or rapid hydrogen atom return to the thiyl radical formed after deprotonation of the corresponding radical cation. Thiolate elimination from the intermediary biradical-zwitterion[7] is suppressed in protic solvents. This was also the case for the β-hydroxylated substrates lysine and threonine.[3]

The product pattern became more complex for the S-alkylated substrates **1b-1d**. The vinylphthalimides **2** (formed by a decarboxylation/elimination sequence) and the thiazinoisoindole carboxylates **4b**, **6b**, **8b** (formed by a PET/deprotonation/cyclization sequence) were produced by ***one*** photochemical event. In contrast to that, the thiazinoindoles **4a**, **6a**, **8a** and the benzazepine-1,5-dione **5** were produced by ***two*** subsequent photochemical steps (*vide infra*). The S-methyl derivative **1b**[8] (eq. 2) mainly gave the tricyclic product **4b** when directly excited or triplet-sensitized by acetone. Under sensitization conditions, however, **2a** and **5** were not formed. As we have already shown for the S-alkylated N-phthaloyl cysteine methyl esters, benzazepines are solely produced from the singlet excited substrates.[5]

Scheme 2

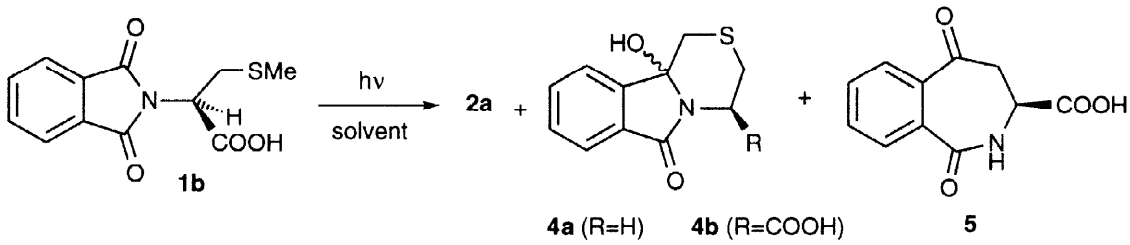


Table 2. Photolysis of **1b** - product composition[b]:

entry	solvent[a]	conversion (%)	**2a** (%)	**4a** (%)	**4b** (%)	**5** (%)
4	acetonitrile	33	12	< 3	66	22
5	acetone	100	< 3	39	61	< 3

[a] 0.01 M solution of **1b** / pyrex / 15°C / 24 h / RPR-208 Rayonet photoreactor;
[b] ^{1}H NMR normalized to 100%.

A similar state dependence concerning the formation of **5** and also the N-vinylphthalimides **2** obviously exists for the free acids **1**. The decarboxylation reaction, when initiated from the excited phthalimide singlet was followed by elimination of methyl thiolate (to give **2a**). In contrast to that, decarboxylation initiated from the phthalimide triplet led to an intermediary open-chain product (**3b**, R=Me) which subsequently underwent PET-cyclization to give the tricyclic product **4a**. This state-selectivity with respect to elimination was also observed for analogous methionine derivatives in our synthetic approach to vinylglycine.[9] Also in case of the S-carboxymethyl substrate **1c** (eq. 3) the elimination reaction (leading to **2a**) played a minor role in the triplet manifold and the annulation reaction (leading to **6b**) was preferred.

Scheme 3

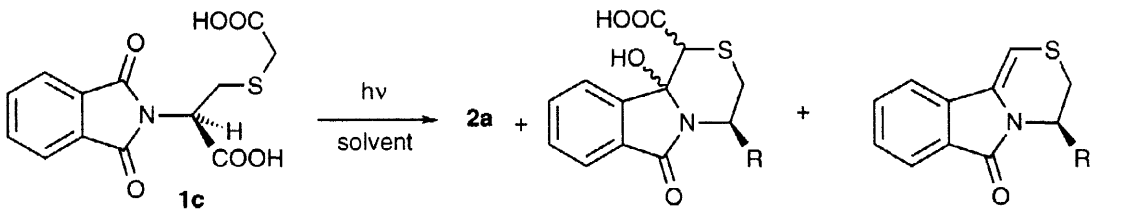


Table 3. Photolysis of **1c** - product composition[b]:

entry	solvent[a]	conversion (%)	**2a** (%)	**6a** (%)	**6b** (%)	**7a** (%)	**7b** (%)
6	acetonitrile	51	78	< 3	< 3	< 3	22
7	acetone	80	15	< 3	21	10	54

[a] 0.01 M solution of **1c** / pyrex / 15°C / 24 h / RPR-208 Rayonet photoreactor;
[b] ^{1}H NMR normalized to 100%.

Much to our surprise, beside the expected PET-cyclization products **6a,b**, two compounds **7a** and **7b** were formed which lacked the carboxy group in the side-chain of the cysteine precursor. The acetone-sensitized reaction even gave **7b** as the major product. It was independently shown that the dicarboxylic acid **6b** is not the precursor to **7a** nor to **7b**, i.e. does not react under the photolysis conditions. Thus, remote decarboxylation preceeds the PET activation of the thioether group for both unsaturated thiazinoisoindoles. This type of radical combination coupled with extrusion of carbon dioxide was described for carboxylic acids activated as the respective carboxylates.[10,11]

Both singlet and triplet excited S-methyl penicillamine **1d** underwent one-photon PET-annulation leading to **8b** (eq. 4). Similar as for **1b,c** the elimination reaction (leading to **2b**) is less effective in the triplet manifold: consequently, a higher amount of two-photon PET-cyclization product **8a** was observed. The *gem* dimethyl substitution protects the substrate from γ-CH cleavage and simplifies the product composition in comparison with the cysteine derivative **1b**.

Scheme 4

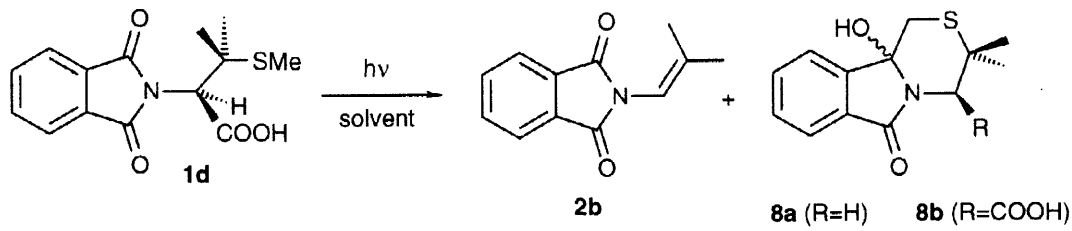


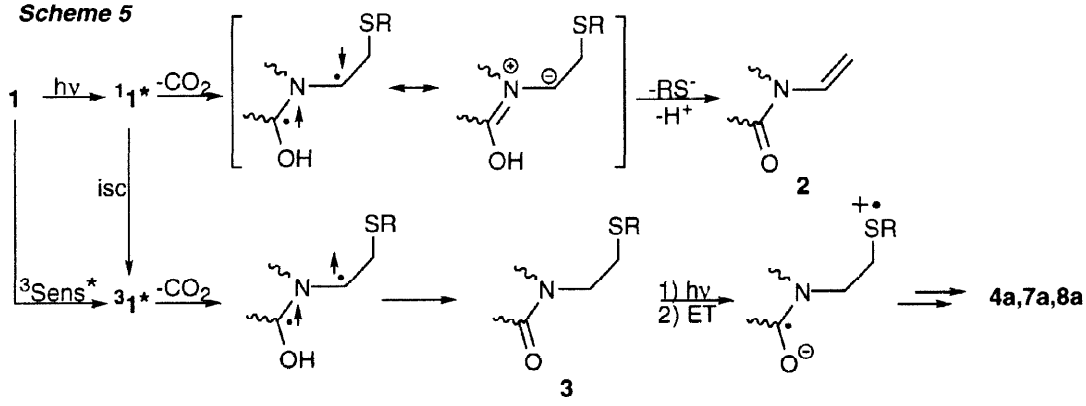
Table 4. Photolysis of **1d** - product composition[b]:

entry	solvent[a]	conversion (%)	**2b** (%)	**8a** (%)	**8b** (%)
8	acetonitrile	17	47	< 3	53
9	acetone	100	9	42	49

[a] 0.01 M solution of **1d** / pyrex / 15°C / 24 h / RPR-208 Rayonet photoreactor;
[b] ^{1}H NMR normalized to 100%.

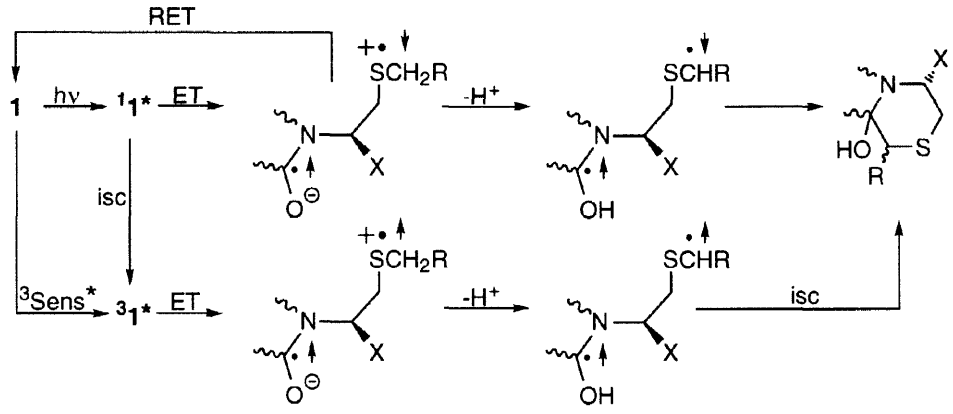
Proposed reaction mechanism. (a) The ratio of elimination to cyclization depends on the multiplicity of the excited phthalimide. This phenomenon is rationalized in Scheme 5. As already indicated before, only the singlet biradical (or zwitterion) which is formed after extrusion of carbon dioxide from the singlet excited **1** seems to be capable of SR^--elimination. The corresponding triplet biradical, prior to elimination of an ionic leaving group, has to undergo intersystem crossing (isc). In competition to this process hydrogen back transfer (intra- or intermolecular) can occur to give **3** which is further electronically excited and eventually gives the cyclization products **4a** and **8a** (and also **7a**, after another photodecarboxylation step). In the presence of proton donors (see the experiments with **1a**, eq. 1), the elimination step is less favorable due to protonation at the stage of the zwitterion.

Scheme 5



(b) The formation of the PET-cyclization products is only slightly dependent on the reaction conditions. This result contrasts our recent findings for the phthaloyl cysteine esters.[5] If, however; the relative conversions were considered, it became obvious that the major contribution to these products comes from the excited phthalimide triplets, whereas the excited singlets preferentially gave return electron transfer (RET). The high efficiency of this energy wasting step becomes apparant from the singlet/triplet quantum yields of substrate consumption measured for the S-methyl-cysteine methyl ester (*vide infra*).

Scheme 6



For the triplet radical ion pairs, product formation can compete with the relatively slow[12] intersystem return electron transfer. The detection of products (**4b**, **6b**, **7b**, **8b**) which derive from sulfur oxidation without subsequent decarboxylation (Scheme 6; X = COOH) is remarkable considering the rapid α-aminoalkyl radical formation reported for the corresponding intermolecular version.[13] As electron acceptor triplet 4-carboxybenzophenone was used in these investigations.[14] On the other hand, decarboxylation is probably not a secondary reaction which proceeds an oxidation of sulfur, at least not for the excited singlets **1a**-**1d**. This is indicated by the fact that the quantum yields for α-decarboxylation of N-phthaloyl amino acids are similar for thioethers (methionine, S-alkyl cysteines) and for the corresponding sulfoxides and sulfones. One exception might be the "remote" decarboxylation observed for the S-carboxymethyl derivative **1c** where sulfur oxidation could precede CO_2 extrusion and formation of the primary thioalkyl radical.

Product/Time-Profile and Quantum Yields of the Photolysis of PHT=Cys(SMe)OMe. (a) The product/time profile of the well-studied N-phthaloyl-S-methylcysteine methyl ester was investigated in order to evaluate the two-photon hypothesis which had been postulated for a while by several research groups for the degradation of N-acyl amino acids via two subsequent Norrish II steps. GC was used for determination of the time profile and GC/MS-MS for product structure elucidation. In no run we were able to detect the postulated intermediate **11**. It is highly probable that this was due to a drastic increased reactivity of the secondary photochemical event, i.e. the formation of thioformaldehyde by a Norrish II cleavage is expected to have a quantum yield near unity. (b) We determined by using valerophenone as a chemical

actinometer the quantum yields for disappearance of **9** and for the formation of products **10**, **12**, **13**, and **14** in acetonitrile and acetone (Scheme 7). For acetone we assumed identical T-T-energy transfer efficiencies from acetone to valerophenone and to the cysteine derivative **9**, respectively.

Scheme 7 (E = COOMe)

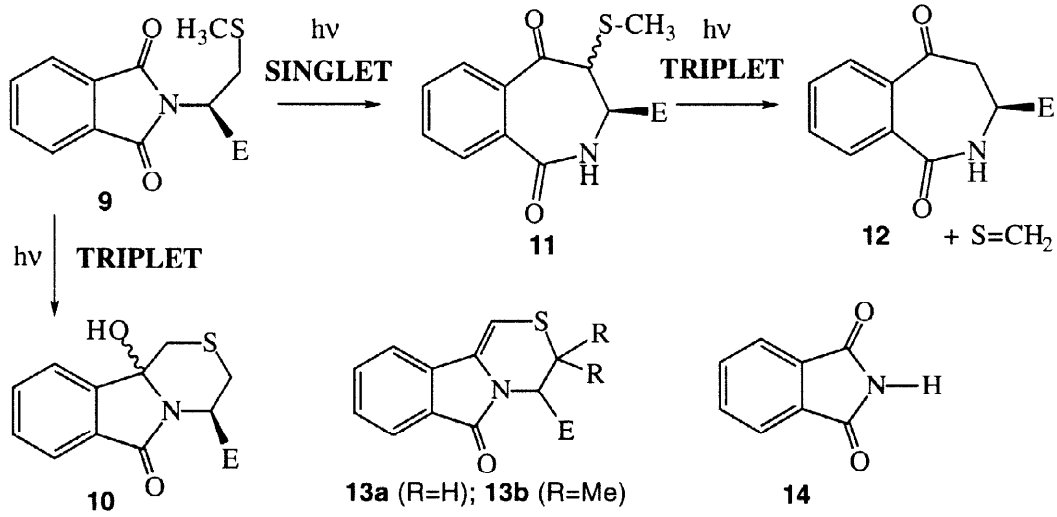


Table 5. Quantum yields[a] for disappearance of **9**[b] / formation of products **10, 12, 13, 14**[b]:

solvent	**9** (%)	**10** + **13a** (%)	**12** (%)	**14** (%)
acetonitrile	< 0.5	-	-	-
acetone	12	8	< 0.5	1

[a] by comparison with valerophenone as chemical actinometer ($\Phi[CH_3CN] = 0.78$)[15]; [b] by GC.

The quantum yield for the disappearance in acetonitrile is remarkably low (< 0.005) in contrast to the value in acetone. This accounts for the assumption that the intersystem crossing efficiency is strongly reduced due to the existence of the electron-donating heteroatom, i.e. the excited singlets are deactivated strongly by an electron transfer/electron return-mechanism. The electon-donating thioether group is essential for this process. Thus, for purely alkyl-substituted amino acid derivatives such as valine or leucine we have detected quantum yields for disappearance (direct irradiation in acetonitrile or benzene) in the range of 0.02 to 0.05, i.e. at least 10 times higher. The quantum yield for triplet reaction is in good agreement with the data for photoinduced electron transfer reactions of sulfide-containing alkyl phenylglyoxylates reported by Hu and Neckers.[16]

EXPERIMENTAL PART

All starting materials (S-alkylated N-phthaloyl amino acids **1** and the methyl ester **9**) were synthesized from enantiomerically pure cysteine and (±)-penicillamine (Degussa AG and Fluka AG) using methods published by Kidd[17], Nefkens[18], and Sheehan.[19]

The photochemical reactions were performed in pyrex vessels (100-250 ml) using a RPR-208 Rayonet® photochemical reactor equipped with 3000Å lamps (approx. 800 W) at 13°C under a nitrogen atmosphere. All solvents used for photoreactions (benzene, acetone, acetonitrile, and methanol) were puriss. p.a. (Fluka). The substrate concentration was varied from 0.01 to 0.05 M. Analyses of the crude product mixtures were performed using ^{1}H and ^{13}C NMR spectroscopy. Product mixtures were separated (when necessary) be means of silica gel column chromatography (Merck, 60-230 mesh). Analyses of the purified photoproducts were performed using ^{1}H and ^{13}C NMR (Bruker AC 200, Bruker AC 250, and Bruker WM 400) spectroscopy, IR (Perkin-Elmer 1420), UV (Hitachi U-3200), and MS (Finnigan MAT 8200) spectroscopy. For product / reaction time profiles GC analyses were performed with a Hewlett-Packard 5890 Series II and a HP-5 capillary column (30 m x 0.32 mm x 0.25 μm film thickness). The following temperature program was used: initial 60°C, held for 1 min; increased from 60°C to 250°C at 20°C/min, held at 250°C for 10 min. The carrier gas (N_2) flow was 1ml/min. The GC-MS measurements were performed with a Finnigan Incos 500 mass spectrometer (Finnigan MAT, San Jose, CA, USA) directly coupled with a Varian 3400 gas chromatograph (Varian Analytical Instruments, Sunnyvale, CA, USA) with a split/splitless injector, and a SE-54 capillary column (25 m x 0.25 mm x 0.25 μm film thickness) (CS-Chromatography Service GmbH Langerwehe, D). The following temperature program was used: initial 70°C, held for 2 min; increased from 70°C to 270°C at 10°C/min, held at 270°C for 8 min. The carrier gas (He) flow was 1ml/min (head pressure 55 kPa). The transfer line temperature was 270°C. The MS was scanned from 50 to 600 u in 1.7 sec. The electron multiplier voltage was 1200 V (EI). GC-MS data were acquired using Data General DG-20.

Standard irradiation procedure

A solution of the substrate (0.01 to 0.05 M) in the appropriate solvent (see Tables 1-3) in a pyrex vessel purged with a constant stream of dry nitrogen was irradiated for 24h. After evaporation of the solvent the composition of the crude product mixture was determined by NMR spectroscopy using the characteristic signals of the independently synthesized compounds and/or purified products.

Determination of quantum yields

A stock solution of the actinometer compound valerophenone in acetonitrile or acetone was irradiated in a Rayonet chamber reactor equipped with 300 nm lamps (ca. 800 W) at 15°C simultaneously with a solution of N-phthaloyl-S-methyl cysteine methyl ester **9** in the corresponding solvent (with identical initial substrat concentration). The ε-values for the substrates at 300 nm were 1674 (**9**) and 39 (valerophenone). The quantum yields for disapperance of **9** were determined in acetonitrile (singlet and triplet paths), acetonitrile in the presence of 10 eq. piperylene (singlet path) and acetone (triplet path) from the slope of the GC traces recalulated to zero conversions and corrected for the ε-values in case of the acetonitrile experiments. The quantum yield for the disapperance of valerophenone is 0.78.[15]

N-Vinylphthalimide (**2a**) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.00 (d, *J* = 9.9 Hz, 1H, =CH), 6.03 (d, *J* = 16.4 Hz, 1H, =CH), 6.83 (dd,*J* = 8.9, 16.4 Hz, 1H, =CH), 7.68 (m, 2H, Ar.-H), 7.80 (m, 2H, Ar-H).- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 104.3 (t), 123.5 (d), 123.8 (d), 131.4 (s), 134.3 (d), 166.3 (s).

N-(2-Methylprop-1-enyl)phthalimide (**2b**)[20] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (d, *J* = 1.3 Hz, 3H), 1.90 (d, *J* = 1.4 Hz, 3H), 5.88 (sept., *J* = 1.4 Hz, 1H, =CH), 7.74 (m, 2H, Ar.-H), 7.85 (m, 2H, Ar.-H).- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 (q), 22.7 (q), 112.1 (d), 123.4 (d), 132.0 (s), 134.1 (d), 139.1 (s), 167.4 (s).

2-Phthalimidoethylmercaptane (**3a**)[21] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 8.0 Hz, 1H), 2.85 (dt, *J* = 7.0, 8.0 Hz, 2H), 3.88 (t, *J* = 7.0 Hz, 2H), 7.68 (m, 2H, Ar.-H), 7.80 (m, 2H, Ar.-H).- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8 (t), 40.7 (t), 123.4 (d), 131.5 (s), 134.1 (d), 167.5 (s).

1,3,4,10b-Tetrahydro-10b-hydroxy-6H-[1,4]thiazino[3,4a]-isoindol-6-one (**4a**) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.54 (m, 2H), 2.69 (d, *J* = 13.5 Hz, 1H), 3.12 (dd, *J* = 1.0, 13.5 Hz, 1H), 3.31 (ddd, *J* = 1.9, 3.8, 13.7 Hz, 1H), 4.38 (ddd, *J* = 2.7, 2.8, 13.7 Hz, 1H), 7.46 (m, 1H, Ar.-H), 7.57 (m, 2H, Ar.-H), 7.69 (m, 1H, Ar.-H).- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.4 (t) 37.5 (t), 38.5 (t), 83.0 (s), 121.6 (d), 123.7 (d), 129.9 (d), 130.9 (s), 132.3 (s), 146.0 (s), 165.0 (s).

1,3,4,10b-Tetrahydro-10b-hydroxy-6H-[1,4]thiazino[3,4a]-isoindol-6-one-4-carboxylate (**4b**) This compound was detected solely in the proton NMR spectrum of the crude reactions mixture. After purification, the corresponding dehydration product **7b** was isolated: significant signals of the diastereoisomers (ca. 60:40) of **4a**: major isomer (probably *trans*): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 (d, J = 13.6 Hz, 1H), 2.76 (dd, *J* = 4.6, 14.2 Hz, 1H), 3.07 (d, *J* = 13.6 Hz, 1H).- minor

isomer (probably *cis*): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (m, 2H), 3.10 (m, 2H).

2,3,4,5-Tetrahydro-1,5-dioxo-1H-benz[c]azepine-3-carboxylate (**5**)[22] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.18 (dd, *J* = 10.7, 18.7 Hz, 1H), 3.29 (dd, *J* = 3.6, 18.8 Hz, 1H), 4.61 (ddd, *J* = 3.7, 5.4, 10.6 Hz, 1H), 7.08 (br., d, *J* = 4.8 Hz, 1H), 7.66 (m, 3H), 7.94 (m, 1H, Ar.-H).

1,3,4,10b-Tetrahydro-10b-hydroxy-6H-[1,4]thiazino-[3,4a]-isoindol-6-one-1-carboxylate (**6a**) This compound was detected solely in the proton NMR spectrum of the crude reactions mixture: characteristic ^{1}H NMR signals (300 MHz, $CDCl_3$): δ = 3.25 (s, 1H, SC<u>H</u>), 4.41 (m, 2H, NC<u>H</u>$_2$).

1,3,4,10b-Tetrahydro-10b-hydroxy-6H-[1,4]thiazino[3,4a]-isoindol-6-one-1,4-dicarboxylate (**6b**) This compound was detected solely in the proton NMR spectrum of the crude reactions mixture. After esterification with MeOH/ HCl, the corresponding dimethyl ester was isolated as a mixture of four diastereoisomers with the significant NC<u>H</u>- ^{1}H NMR signals (300 MHz, $CDCl_3$): δ =5.58 (dd, *J* = 2.0, 5.0 Hz), 5.45 (dd, *J* = 2.4, 4.8 Hz), 4.82 (dd, *J* = 3.4, 6.0 Hz), 4.49 (dd, *J* = 2.6, 11.8 Hz).- $C_{15}H_{15}NO_6S$ (337.3) calc. C 53.41, H 4.48, N 4.15, S 9.50, calc. C 53.19, H 4.54, N 4.33, S 9.29. Dehydration of this compound via treatment with trifluoroacetic acid led to the corresponding eneamide: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.20 (dd, *J* = 3.5, 13.2 Hz, 1H), 3.53 (dd, *J* = 3.1, 13.2 Hz, 1H), 3.70 (s, 3H), 3.91 (s, 3H), 5.60 (dd, *J* = 3.1, 3.5 Hz, 1H), 7.59 (m, 4H, Ar.-H).- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.4 (t), 51.1 (q), 52.9 (q), 53.3 (d), 107.6 (s), 123.4 (d), 126.1 (d), 128.0 (s), 133.9 (s), 136.1 (s), 164.2 (s), 166.0 (s), 168.0 (s).

3,4-Dihydro-6H-[1,4]thiazino[3,4a]isoindol-6-one (**7a**)[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.40 (m, 2H), 4.42 (dd, *J* = 3.3, 3.3 Hz, 2H), 6.10 (s, 1H, =CH), 7.48 (m, 1H, Ar.-H), 7.58 (m, 2H, Ar.-H), 7.84 (m, 1H, Ar.-H).

3,4-Dihydro-6H-[1,4]thiazino-[3,4a]isoindol-6-one-4-carboxylate (**7b**) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.25 (dd, *J* = 3.3, 13.1 Hz, 1H), 3.50 (ddd, *J* = 2.4, 3.3, 13.1 Hz, 1H), 5.50 (dd, *J* = 3.3, 3.3 Hz, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 7.48 (m, 1H, Ar.-H), 7.58 (m, 2H, Ar.-H), 7.84 (m, 1H, Ar.-H)- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.8 (t), 51.2 (d), 100.8 (d), 119.0 (d), 123.5 (d), 126.8 (s), 128.5 (d), 131.1 (s), 132.3 (d), 134.3 (s), 166.2 (s), 171.4 (s).

1,3,4,10b-Tetrahydro-10b-hydroxy-3,3-dimethyl-6H-[1,4]thiazino[3,4a]-isoindol-6-one (**8a**) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 3H), 1.33 (s, 3H), 2.91 (d, *J* = 13.8 Hz, 1H), 3.05 (d, *J* = 13.9 Hz, 1H), 3.21 (d, *J* = 13.4 Hz, 1H), 3.99 (d, *J* = 13.4 Hz, 1H), 5.55 (br. s, 1H), 7.54-7.73 (m, 4H, Ar.-H).- ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.3 (q), 26.7 (q), 35.8 (t), 40.4 (s), 49.0 (s), 82.4 (s), 121.7 (d), 123.8 (d), 129.9 (d), 130.7 (s), 132.3 (d), 134.2 (s), 165.6 (s).

1,3,4,10b-Tetrahydro-10b-hydroxy-3,3-dimethyl-6H-[1,4]thiazino[3,4a]-isoindol-6-one-4-carboxylate (**8b**) from entry 8 was esterified with methanol/HCl[5] and isolated as the corresponding dehydration product **13b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (s, 3H), 1.55 (s, 3H), 3.71 (s, 3H), 4.97 (s, 1H), 6.53 (s, 1H, =CH), 7.44 (m, 2H, Ar.-H), 7.58 (m, 2H, Ar.-H), 7.86 (d, *J* = 9.7 Hz, 1H, Ar.-H).- ^{13}C- NMR (75 MHz, $CDCl_3$): δ = 29.4 (q), 30.9 (q), 43.9 (s), 53.4 (s), 53.4 (q), 60.5 (d), 104.9 (d), 107.8 (s), 111.5 (s), 117.2 (s), 119.4 (d), 123.8 (d), 133.3 (d), 159.1 (s), 160.8 (s).

Compounds **9**, **10**, **13a** and **14** are described in ref. 5.

MS-data: **9** (EI, 70eV): *m/z* 279 (M^+, 5%), 132 (100%), 220 ((M-COOMe)$^+$, 10%), 232 ((M-SMe)$^+$, 5%); **10** (EI, 70eV): *m/z* 261 (M^+, 45%), 202 ((M-COOMe)$^+$, 100%); **12** (EI, 70eV): *m/z* 233 (M^+, 5%), 174 ((M-COOMe)$^+$, 100%), 147 (55%); **12** (CI, CH_4): *m/z* 234 (M^++H, 18%), 262 ((M+C_2H_5)$^+$, 5%); **14** (EI, 70eV): *m/z* 147 (M^+, 100%), 104 (50%), 76 (45%).

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