Functionalized Imides by Regioselective Ozonation

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Ozonations of alkoxy- and (acyloxy)-substituted alkylidene-lactams **1** and **5** or of the alkylidene-sultams **9** and **10** proceeded by regioselective cleavage of the exocyclic C=C bonds (*Schemes 1* and *2*). These bonds are part of an enamide system and, therefore, possess considerable polarity as shown by ^{13}C-NMR spectra. As a result, the partly known maleimides **3** and **6** or the 'sulfonimides' **11** were obtained. Compounds **3** and **11** reacted with diazomethane to give the highly reactive bicyclic derivatives **8** and **12**, respectively. The cinnamylidene-lactames **16a**,**b** were converted by selective ozonolysis mainly into the formylmethylene lactames **17a**,**b** (*Scheme 3*). The amino-substituted aldehyde **20** bears a structural relationship to the lactone antibiotic basidalin **21a**. The tendency of some donor-substituted maleimides to undergo [2+2] cycloadditions was assessed (*Scheme 4*). The configuration of the photodimers **22a**,**b** and **24a**,**b** was established by X-ray crystallography.

Introduction. – The cleavage of alkene C=C bonds by ozone to give aldehydes, ketones, and carboxylic acids was introduced into organic chemistry at the beginning of the 20th century by *Harries* [1]. Ozonolyses take place under extremely mild reaction conditions and often with excellent yields. The individual course of an ozonization, however, is strongly dependent on the constitution of the starting material, the solvent, and the choice of reductive or oxidative workup conditions (for a comprehensive review, see [2]).

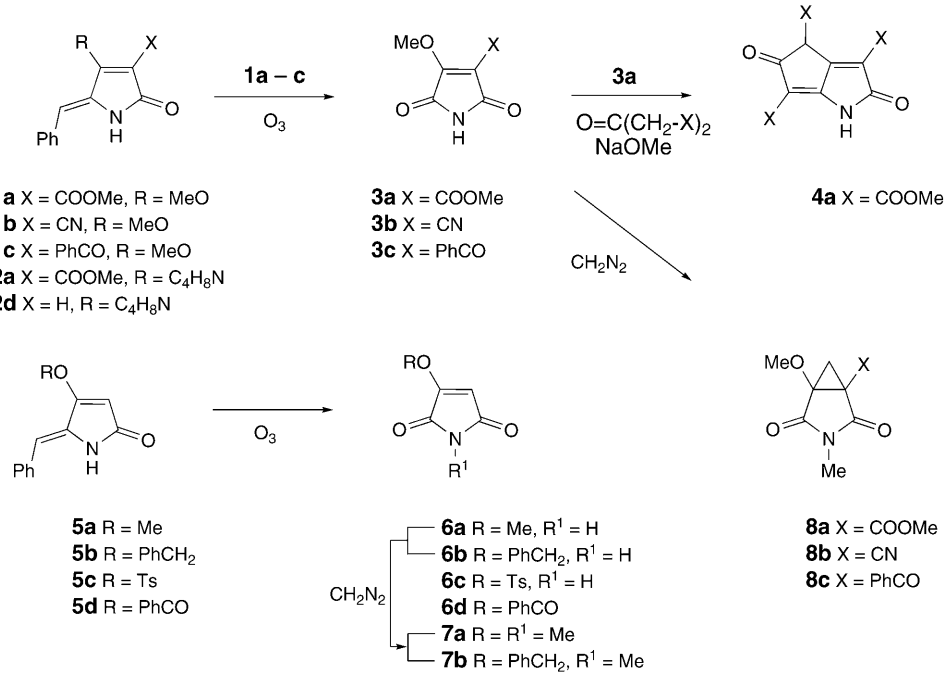
A basic three-step mechanism was formulated by *Criegee* and is now bearing his name [3]. In a sequence of concerted 1,3-dipolar cycloaddition and cycloreversion, 'carbonyl oxides' [4] are formed which are captured by internally generated carbonyl compounds in another 1,3-dipolar cycloaddition to yield ozonides. As a result, for unsymmetrical alkenes, substituent rules for the regioselective O–O splitting in the cycloreversion step have been formulated [5][6]. There are, however, exceptions from these rules, and the ozonide-forming step may be bypassed due to low dipolarophilicity of the carbonyl intermediate. Both is examplified in the ozonolysis of ketene acetals [7]. Modifications of the original *Criegee* mechanism have been introduced later [8]. An alternative mechanistic concept of ozonations was recently brought up for discussion [9]. According to the 'donor-acceptor concept', ozonations are regarded as oxidation reactions with radical-ion intermediates.

It is well known that the C=C bond of enol ethers is readily cleaved by ozone forming a carbonyl compound and a carboxylic acid ester [10–14]. Analogously, in the ozonolysis of enol esters, beside a carbonyl compound, a mixed carboxylic acid anhydride is

formed [7][15]. The C=C bonds of enamines can be more resistant towards ozone than those of structurally related enol ethers [15]. We made deviating observations in the course of ozonations of the lactams **1** bearing an enol ether moiety, and the lactams **2** with an enamine partial structure. These ozonolyses were carried out for synthetic purposes.

Results and Discussion. – Ozonation of the lactams **1** in nonparticipating solvents furnished the maleimides **3a**–**c** (*Scheme 1*). Maleimides **3a** and **3b** have been synthesized previously on another route [16]. The lactams **1a**–**c** contain conjugated exocyclic and endocyclic C=C bonds. Only the former ones were attacked by ozone.

Scheme 1



Regarding the π-system of lactams **1**–**3** comprising the heterocycle and the exocyclic C=C bond, one is tempted to depict zwitterionic pyrrole resonance structures with positive charges at the respective H*C*=C(5) (in short C(α)) atoms. This view, however, is ruled out by the ^{13}C-NMR spectra of these compounds. For instance, the signal of C(α) of **1a** was found at δ 109.0. This highfield shift, indicating an increased electron density at C(α), was present in the ^{13}C-NMR spectra of all lactams used here. Hence, most of all, the enamide substructures of the lactams determine their reactivity.

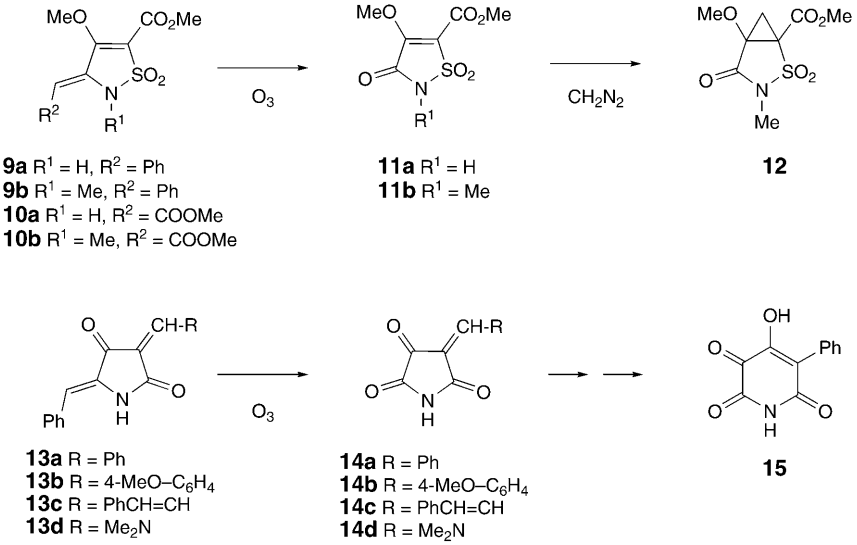
Because of the pyrrolidin-1-yl substituent, the lactam ring in compounds **2** is more electron-rich than in the lactams **1**. Ozonation of compounds **2** afforded no crystalline products so that apparently both C=C bonds were cleaved by ozone. In contrast to that, ozonation of the vinylogous esters **5a** and **5b** caused selective cleavage of the exocyclic

C=C bond to yield the maleimides **6a**,**b**. Both compounds reacted with diazomethane to give the *N*-methylated derivatives **7a**,**b** as already described for **7a** a long time ago [17]. With the vinylogous anhydrides **5c**,**d**, again regioselective ozonolysis was observed. Only the exocyclic C=C bond was cleaved to furnish the maleimides **6c**,**d**.

The donor–acceptor-substituted maleimides **3** are starting materials for the synthesis of different bicyclic compounds. Compound **3a** reacted with dimethyl 3-oxopentanedioate in the presence of MeONa or NaH to give the red anion of the bicyclic lactam **4a** by successive ester condensation and *Michael* addition. When treated with diazomethane in excess, the enol ethers **3a**–**c** were converted into the bicyclic imides **8a**–**c** by *N*-methylation and subsequent cyclopropanation. The imides **8a**,**b** and their use for the synthesis of functionalized pyridinones by ring expansion have recently been described by us [16]. In this context we were interested to synthesize 'sulfonimides' as heteroanalogs of the imides **3a** and **8a**.

As starting material served the sultams **9a**,**b** (*Scheme 2*). Compound **9a** has been synthesized earlier [18]. *N*-Methylation of **9a** to **9b** was accomplished by diazomethane in excess or by heating of **9a** with tetramethyl orthocarbonate. Because of the structural similarity of the alkylidene-sultams **9a**,**b** and the alkylidene-lactam **1a**, we were not surprised that selective ozonolysis of **9a**,**b** took place furnishing the 'sulfonimides' **11a**,**b**. The same compounds were obtained by ozonation of the sultams **10a**,**b** [19] (*Scheme 2*).

Scheme 2



9a R^1 = H, R^2 = Ph
9b R^1 = Me, R^2 = Ph
10a R^1 = H, R^2 = COOMe
10b R^1 = Me, R^2 = COOMe

11a R^1 = H
11b R^1 = Me

12

13a R = Ph
13b R = 4-MeO–C_6H_4
13c R = PhCH=CH
13d R = Me_2N

14a R = Ph
14b R = 4-MeO–C_6H_4
14c R = PhCH=CH
14d R = Me_2N

15

The analogous behavior of both types of sultams in this reaction is notable in the light of the highly different polarity of the exocyclic C=C bond in the benzylidene-sultams **9a**,**b** on the one hand, and in the differently substituted alkylidene-sultams **10a**,**b** on the other hand. The ^{13}C-NMR signal of C(α) in compound **9b** was found at δ 115.2, *i.e.*, a value fairly in line with the corresponding signal of lactam **1a**, whereas the signal of C(α) of sultam **10b** was shifted further highfield to δ 91.0. Concomitantly the ^{1}H-

NMR signal of the olefinic H-atom of **10b** appeared at δ 5.55 [19]. This signal disappeared upon addition of D_2O. This H/D exchange is apparently due to the high polarity of the ene-sulfamide partial structure. Treatment of both new imides **11a**,**b** with diazomethane in excess produced the highly reactive bicyclic sultam **12**.

The above described regioselective ozonolyses of readily available tetramates and of heterologous sultams enriches the known methods for the production of functionalized maleimides by amination of maleic anhydrides [20] [21] or by ester condensation [18][22]. 'Sulfonimides' likewise have been prepared by ester condensation [18] even though they were usually synthesized by *S*-oxidation of isothiazol-3(2*H*)-ones [23].

Regioselective ozonolysis was also observed with the easily accessible α,γ-bis(alkylidene)lactams **13a**–**c**. We obtained the succinimides **14a**–**c** in yields of 60–75% (*Scheme 2*). Similarly the [(dimethylamino)methylene]lactam **13d** was converted into imide **14d**. Apparently, we have at hand a useful method for the preparation of variably substituted alkylidenepyrrolidine-2,3,5-triones. Such substances are interesting because they can be converted into persubstituted pyridinones in a few steps, as already shown by the conversion of the benzylidene compound **14a** into the pyridine derivative **15** [24]. In addition, compounds of type **14** have been used for the preparation of different types of heterocycles by cycloaddition or cyclocondensation reactions [25].

In all the ozonations mentioned above, a reductive or oxidative workup was unnecessary. The second product of the cleavage of all benzylidenelactams was benzoic acid which originated either from oxidation of the firstly formed benzaldehyde by peroxidic intermediates or was the result of an 'ozonide-free reaction'.

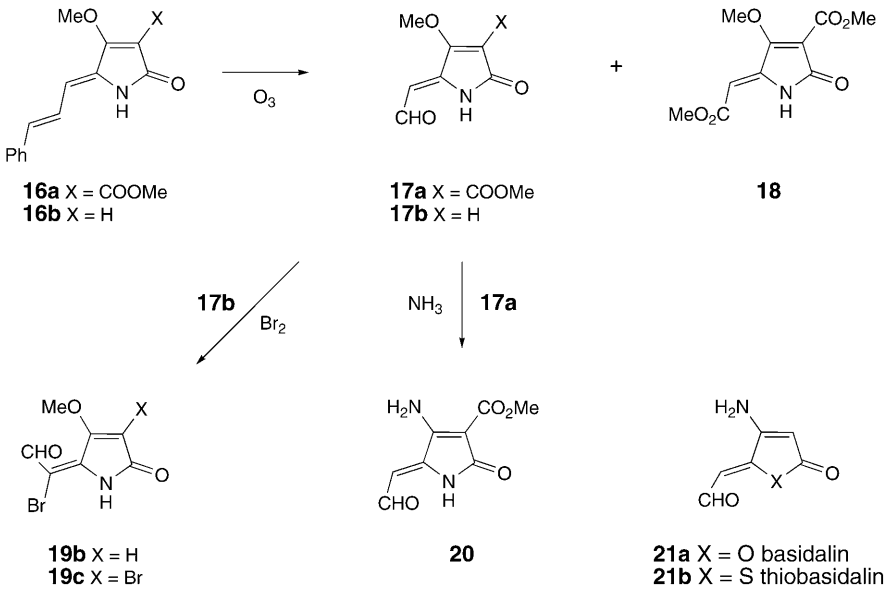
Finally, we were interested to find out how the cinnamylidenelactams **16** [26] and ozone might interact. It turned out that in both **16a** and **16b**, selectively the terminal C=C bond of the side chain was cleaved (*Scheme 3*). Beside benzoic acid, we obtained the aldehydes **17a** or **17b**, respectively, as the main products. The (*Z*)-configuration of the new compounds was assigned by the NOE data. Presumably, this configuration is stabilized by H-bonding interactions.

If the ozonolysis of **16a** was conducted in the presence of MeOH, beside aldehyde **17a**, surprisingly ester **18** was isolated, although the amount was very small. Compound **18** was synthesized on an independent route [18] so that the structure of this by-product is beyond any doubt. The (relative) ozone-resistance of the alkylidenelactam **18** contrasts with the ozone-sensibility of the identically substituted sultam **10a**. In addition, the ozone-resistance of compounds **17**/**18** in contrast to the reactivity of **1a** is remarkable. The structural similarity of both types of alkylidenelactams is reflected in the similarity of their ^{13}C-NMR spectra.

The aldehydes **17a**,**b** have shown substantial antimycobacterial activity [27]. This makes it worthwhile to emphasize the structural similarity of these compounds to the lactone antibiotic basidalin (**21a**) [28]. Efforts to synthesize this compound yielded only the stereoisomeric (*E*)-basidalin [29]. On the other hand, the thio analog of basidalin, **21b**, has been prepared and found to be cytotoxic [30]. The aldehydes **17a**/**b** may be useful for the preparation of 'azabasidalin' and derivatives. An entry to this goal offers compound **20** which was obtained from aldehyde **17a** and ammonia (*Scheme 3*).

The configuration of the aldehydes **17** may be altered by substituents in the side chain. Bromination of **17b** led to disubstitution in two separate steps (*Scheme 3*). At first, the side-chain-brominated aldehyde **19b** was obtained. The (*Z*)-configuration

Scheme 3



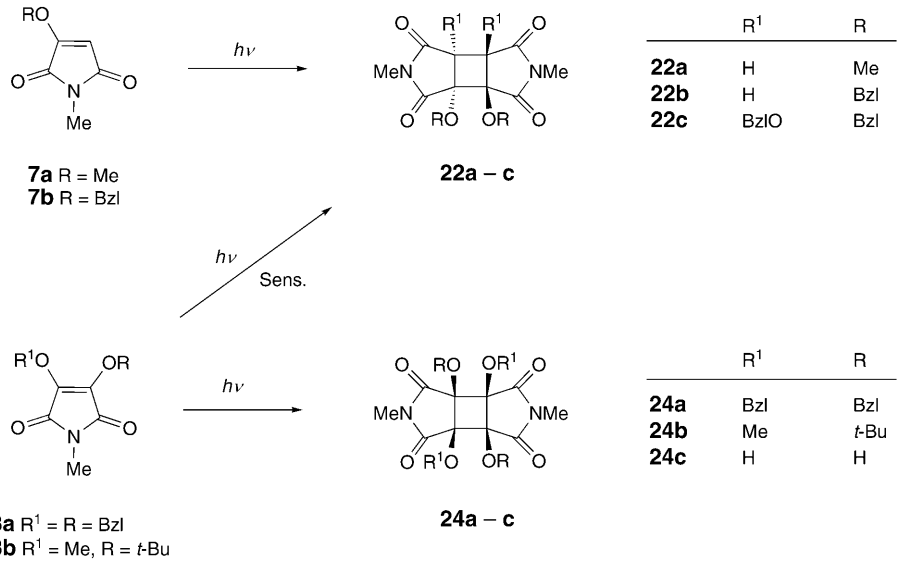
was established by NOE experiments. Further bromination of **19b** furnished aldehyde **19c**. These aldehydes or suitable derivatives may allow ring-closure reactions.

Handling the donor-substituted maleimides **6a**,**b** and especially **7a**,**b**, we observed that these substances undergo changes upon influence of light. From solutions of **7a**,**b**, we obtained the uniform photodimers **22a**,**b** after standing for 2–3 weeks in daylight or after a short-time exposure to UV light (*Scheme 4*). Single-crystal X-ray analyses revealed that in both cases, head-to-head additions had taken place forming the cyclobutanes **22a**[1]) and **22b**[1]) with the alkoxy substituents arranged in *trans* position.

The light-induced cycloaddition of a few maleic anhydrides and maleimides has been described [31]. However, usually the presence of a radiation sensitizer was required. Sensitizers are needed also in the photodimerization of vinyl ethers [32][33]. So the ease of the photoreaction of the donor-substituted maleimides **7a**,**b** is indeed surprising. Therefore, we have looked at the behavior toward light of similar maleimides at hand. No tendency toward dimerization in light was observed on irradiation of the donor–acceptor-substituted maleimides **3** or the (acyloxy)-substituted maleimides **6c**,**d**. The opposite was true for maleimides **23a**,**b** [34] with two donor substituents. Imide **23a** in solution was converted by UV light mainly into the photodimer **24a**. As established by X-ray crystallography[1]) all four benzyloxy groups of **24a** are in *cis* position to each other. However, if imide **23a** was exposed to light in the presence of traces of benzophenone as radiation sensitizer, the isomeric dimer **22c** was obtained. Irradiation of a solution of the differently substituted imide **23b** without a sensitizer

[1]) CCDC-291584 (**22a**), CCDC-291585 (**22b**), CCDC-291541 (**24a**), and CCDC-291586 (**24b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* www.ccdc.cam.ac.uk/data_request/cif.

Scheme 4



led to the cyclobutane **24b** as head-to-tail cyclodimerization product with all MeO and *t*-BuO substituents arranged in *cis* position[1]). Catalytic debenzylation of compound **24a** yielded the *all-cis* tetrahydroxy derivative **24c**.

Experimental Part

General. Ozone was generated by the *Ozongenerator Fischer 502*°, capacity: 4.3 g ozone/h at an O_2 flow rate of 60 l/h. Photochemical reactions were run in a reactor equipped with a high-pressure mercury vapor immersion lamp (*HPK 125, Philips*), 125 W. CC: Flash column 250 ml (*Baker*); silica gel 0.040–0.063 mm (*Merck*). M.p.: *Büchi-B-540* apparatus; uncorrected. UV Spectra: MeOH soln. if not stated otherwise; *Perkin-Elmer-Lambda-20* or *Jasco-V-530* spectrometer; λ_{max}(log ε) in nm. IR Spectra: KBr plates; *Paragon-1000* a FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Jeol-Elipse-400* or *Jeol-Elipse-500* FT spectrometer; in (D_6)DMSO if not indicated otherwise; δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. MS: *Hewlett-Packard-5989A* (EI (70 eV) and CI), *Jeol-JMS-GCMATE-II* (HR), and *Sciex-API-2000* (ESI) spectrometer; in *m*/*z*. Microanalyses: *CHN Analyzer Elementar Vario EL*.

Ozonation: *General Procedure* (*G.P.*). A stream of O_3 (60 l/h) was passed through a soln. of the respective substance (2–5 mmol) in 100 ml of CH_2Cl_2 (*G.P. A*) or in CH_2Cl_2/MeOH 1:1 (*G.P. B*) at −15° for 4 min (*ca.* 6 mmol O_3). The solvent was partly evaporated at a temp. not exceeding 10° (*caution:* potential decomposition of highly explosive by-products). The residue (5–10 ml) was diluted with an equal volume of Et_2O or AcOEt and kept in the refrigerator for crystallization.

*5-Benzylidene-2,5-dihydro-4-methoxy-2-oxo-1*H*-pyrrole-3-carboxylic Acid Methyl Ester* (**1a**) [26]. ^{1}H-NMR: 10.19 (*s*, 1 H); 7.61–7.32 (*m*, 5 H); 6.41 (*s*, 1 H); 4.08 (*s*, MeO); 3.76 (*s*, COOMe). ^{13}C-NMR: 167.8 (C(4)); 164.6, 163.1 (C=O); 133.5–128.3 (C(5), arom. C); 109.0 (CH=); 100.1 (C(3)); 61.0 (MeO); 52.1 (COOMe).

*3-Benzoyl-5-benzylidene-1,5-dihydro-4-methoxy-2*H*-pyrrol-2-one* (**1c**). An Et_2O soln. of diazomethane (excess) was added to a suspension of 3-benzoyl-5-benzylidene-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one [35] (0.58 g, 2 mmol) in MeOH (5 ml). After the evolution of N_2 had ceased, the soln. was evaporated and the residue crystallized from MeOH: 0.45 g (74%) of **1c**. Light yellow crystals. M.p.

197°. UV: 337 (4.392). IR: 3218, 1675, 1642, 1577. ^{1}H-NMR ($CDCl_3$): 8.62 (*s*, 1 H); 8.05–7.90 (*m*, 2 H); 7.65–7.15 (*m*, 8 H); 6.50 (*s*, 1 H); 3.95 (*s*, 3 H). Anal. calc. for $C_{19}H_{15}NO_3$ (305.33): C 74.74, H 4.95, N 4.58; found: C 74.62, H 4.87, N 4.49.

*5-Benzylidene-2,5-dihydro-2-oxo-4-(pyrrolidin-1-yl)-1*H*-pyrrole-3-carboxylic Acid Methyl Ester* (**2a**). Pyrrolidine (0.5 ml) was added to a soln. of **1a** [26] (0.26 g, 1 mmol) in MeOH (30 ml). Shortly thereafter, yellowish crystals started to separate: 0.24 g (80%) of **2a**. M.p. 149° (MeOH). UV: 326 (4.347). IR: 3201, 1659, 1622, 1551. ^{1}H-NMR: 9.21 (br., 1 H); 7.55–7.28 (*m*, 5 H); 6.56 (*s*, 1 H); 3.66 (*s*, 3 H); 3.59 (*m*, 4 H); 1.94 (*m*, 4 H). ^{13}C-NMR: 168.7 (C(4)); 164.6, 154.7 (C=O); 134.7–127.5 (C(5), arom. C); 112.1 (CH=); 93.6 (C(3)); 53.7 (CH_2N); 51.1 (MeO); 25.3 (CH_2). Anal. calc. for $C_{19}H_{15}NO_3$ (298.34): C 68.44, H 6.08, N 9.39; found: C 68.34, H 6.27, N 9.24.

*5-Benzylidene-1,5-dihydro-4-(pyrrolidin-1-yl)-2*H*-pyrrol-2-one* (**2d**). Under stirring, compound **2a** (0.90 g, 3 mmol) was heated with freshly prepared *t*-BuOK (2.8 g, 25 mmol) in DMSO (15 ml) to 80° for 1 h. The precipitate was filtered off and then dissolved in H_2O, the soln. acidified with 2N HCl, and the crude product collected and recrystallized from ^{i}Pr$_2$O/MeOH: 0.57 g (80%) of **2d**. Yellow crystals. M.p. 186°. UV: 226 (4.220), 317 (4.355), 375 (br.). IR: 3250, 2960, 2860, 1655, 1535. ^{1}H-NMR: 8.87 (*s*, 1 H); 7.58–7.25 (*m*, 5 H); 6.31 (*s*, 1 H); 4.64 (*s*, 1 H); 3.46 (*m*, 4 H); 1.97 (*m*, 4 H). ^{13}C-NMR: 172.4 (C(4)); 156.0 (C=O); 134.9–127.0 (C(5), arom. C); 108.6 (CH=); 88.4 (C(3)); 50.8 (CH_2N); 25.1 (CH_2). Anal. calc. for $C_{15}H_{16}N_2O$ (240.31): C 74.97, H 6.71, N 11.66; found: C 75.08, H 6.50, N 11.38.

*2,5-Dihydro-4-methoxy-2,5-dioxo-1*H*-pyrrole-3-carboxylic Acid Methyl Ester* (**3a**). According to the *G.P. A*, from **1a** [26] (1.0 g, 3.8 mmol). Crystallization started after addition of AcOEt: 0.37 g (52%) of **3a**. M.p. 155° (AcOEt) ([16]: 155°). ^{1}H-NMR: 11.07 (*s*, 1 H); 4.19 (*s*, 3 H); 3.74 (*s*, 3 H). ^{13}C-NMR: 167.9 (C(4)); 165.5, 161.3, 159.9 (C=O); 103.0 (C(3)); 61.6 (MeO); 52.5 (COOMe). MS: 185 (M^+). Anal. calc. for $C_7H_7NO_3$ (185.14): C 45.41, H 3.81, N 7.57; found: C 45.27, H 3.80, N 7.47.

*2,5-Dihydro-4-methoxy-2,5-dioxo-1*H*-pyrrole-3-carbonitrile* (**3b**). According to the *G.P. A*, from **1b** [16] (1.0 g, 4.4 mmol): 0.36 g (60%) of **3b**. M.p. 189–190° ([22]: 190°).

*3-Benzoyl-4-methoxy-1*H*-pyrrole-2,5-dione* (**3c**). According to *G.P. A*, from **1c** (0.90 g, 3 mmol). Crystallization started after addition of Et_2O: 0.30 g (43%) of **3c**. M.p. 148° (^{i}Pr$_2$O/EtOH). UV: 247 (3.679), 308 (3.481). IR: 3227, 1788, 1740, 1655. ^{1}H-NMR ($CDCl_3$): 10.56 (*s*, 1 H); 7.95–7.87 (*m*, 2 H); 7.72–7.50 (*m*, 3 H); 4.01 (*s*, 3 H). Anal. calc. for $C_{12}H_9NO_4$ (231.21): C 62.34, H 3.92, N 6.06; found: C 62.24, H 3.92, N 5.93.

*1,2,4,5-Tetrahydro-2,5-dioxocyclopenta[*b*]pyrrole-3,4,6-tricarboxylic Acid Trimethyl Ester* (**4a**). NaH (0.80 g, 60%, 20 mmol) was added to a stirred soln. of 3-oxopentanedioic acid dimethyl ester (1.74 g, 10 mmol) in THF (50 ml). After the evolution of H_2 had ceased, **3a** (1.81 g, 10 mmol) was added in portions. The red suspension obtained within 30 min was evaporated. The aq. soln. of the residue (75 ml) was acidified with 2N HCl (10 ml) and extracted twice with CH_2Cl_2 (75 ml). The org. phase was dried (Na_2SO_4) and evaporated and the oily residue dissolved in Et_2O (20 ml) and set aside for crystallization in the refrigerator: 0.66 g (22%) of **4a**. Beige crystals. M.p. 220° (dec.). UV: 223 (4.195), 279 (4.388), 325 (4.158). IR: 3220, 2970, 2925, 1750, 1730, 1670, 1640. ^{1}H-NMR: 11.96 (*s*, exchange with D_2O, 1 H); 4.56 (*s*, exchange with D_2O, 1 H); 3.94 (*s*, 6 H); 3.81 (*s*, 3 H). MS: 309 (M^+). Anal. calc. for $C_{13}H_{11}NO_8$ (309.23): C 50.49, H 3.59, N 4.53; found: C 50.56, H 3.71, N 4.70.

*5-Benzylidene-1,5-dihydro-4-methoxy-2*H*-pyrrol-2-one* (**5a**) [26]. ^{1}H-NMR: 9.73 (br., 1 H); 7.55–7.23 (*m*, 5 H); 6.16 (*s*, 1 H); 5.33 (*d*, *J* = 1.5, 1 H); 3.89 (*s*, 3 H). ^{13}C-NMR: 171.7 (C(4)); 167.1 (C=O); 133.8–127.5 (C(5), arom. C); 105.5 (CH=); 92.5 (C(3)); 58.4 (MeO).

*5-Benzylidene-4-(benzyloxy)-1,5-dihydro-2*H*-pyrrol-2-one* (**5b**). A soln. of 5-benzylidene-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one [26] (1.87 g, 10 mmol) in toluene (50 ml) and benzyl alcohol (10 ml) were refluxed in the presence of TsOH (0.34 g, 2 mmol). After 3 h, the mixture was evaporated and the residue recrystallized from AcOEt: 1.50 g (54%) of **5b**. Light yellow crystals. M.p. 156°. UV: 321 (4.416). IR: 3206, 1694, 1587. ^{1}H-NMR ($CDCl_3$): 7.65 (*s*, 1 H); 7.43–7.23 (*m*, 10 H); 6.37 (*s*, 1 H); 5.26 (*d*, *J* = 1, 1 H); 5.09 (*s*, 2 H). Anal. calc. for $C_{18}H_{15}NO_2$ (277.33): C 77.96, H 5.45, N 5.05; found: C 77.73, H 5.53, N 5.18.

*5-Benzylidene-1,5-dihydro-4-{[(4-methylphenyl)sulfonyl]oxy}-2*H*-pyrrol-2-one* (**5c**). The 5-benzylidene-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one [26] (1.87 g, 10 mmol) was added to a freshly prepared NaOMe soln. (0.23 g (10 mmol) of Na) in MeOH (50 ml). The soln. was cooled to 0°. Under stirring,

TsCl (2.1 g, 11 mmol) was added in portions. After a short time, the product started to crystallize: 2.90 g (85%) of **5c**. Yellowish crystals. M.p. 147°. UV: 228 (4.352), 338 (4.405). IR: 3200, 1705, 1651, 1594. ^{1}H-NMR ($CDCl_3$): 8.05 (*s*, 1 H); 7.90–7.86 (*m*, 2 H); 7.42–7.30 (*m*, 7 H); 6.21 (*s*, 1 H); 5.86 (*d*, *J* = 2, 1 H); 2.45 (*s*, 3 H). Anal. calc. for $C_{18}H_{15}NO_4S$ (341.39): C 63.33, H 4.43, N 4.10; found: C 63.74, H 4.58, N 4.00.

*4-(Benzoyloxy)-5-benzylidene-1,5-dihydro-2*H*-pyrrol-2-one* (**5d**) [36]. ^{1}H-NMR: 10.26 (*s*, 1 H); 8.26 (*d*, *J* = 8, 2 H); 7.81 (*s*, 1 H); 7.70–7.64 (*m*, 5 H); 7.42–7.33 (*m*, 3 H); 6.53 (*s*, 1 H); 6.23 (*s*, 1 H). ^{13}C-NMR: 170.6, 161.9 (C=O); 155.6 (C(4)); 134.9–127.7 (C(5), arom. C); 108.1 (CH=); 105.6 (C(3)).

*3-Methoxy-1*H*-pyrrole-2,5-dione* (**6a**). According to the *G.P. A*, from **5a** [26] (1.0 g, 5 mmol): 0.28 g (50%) of **6a**. M.p. 168° ([17a]: 169°). ^{1}H-NMR: 5.73 (*d*, *J* = 1.5, 1 H); 3.87 (*s*, 3 H). ^{13}C-NMR: 171.3 (C(4)); 166.7, 160.9 (C=O); 97.7 (C(3)); 59.1 (MeO).

*3-(Benzyloxy)-1*H*-pyrrole-2,5-dione* (**6b**). According to the *G.P. A*, from **5b** (1.0 g, 3.6 mmol): 0.30 g (41%) of **6b**. Colorless crystals. M.p. 160° (MeOH). UV: 226 (4.227). IR: 3107, 1764, 1742, 1702, 1635. ^{1}H-NMR ($CDCl_3$): 7.45–7.35 (*m*, 5 H); 5.44 (*d*, *J* = 1.5, 1 H); 5.10 (*s*, 2 H). Anal. calc. for $C_{11}H_9NO_3$ (203.20): C 65.02, H 4.46, N 6.89; found: C 65.22, H 4.57, N 6.98.

*3-{[(4-Methylphenyl)sulfonyl]oxy}-1*H*-pyrrol-2,5-dione* (**6c**). According to the *G.P. B*, from **5c** (1.0 g, 3 mmol): 0.40 g (50%) of **6c**. Colorless crystals. M.p. 160° (MeOH). UV: 224 (4.391). IR: 3210, 1803, 1729, 1627. ^{1}H-NMR: 11.14 (br., 1 H); 8.02/7.56 (*d*, *J* = 8, 4 H); 6.45 (*d*, *J* = 2, 1 H); 2.45 (*s*, 3 H). Anal. calc. for $C_{11}H_9NO_5S$ (267.26): C 49.44, H 3.39, N 5.24; found: C 49.21, H 3.71, N 5.13.

*4-(Benzoyloxy)-1*H*-pyrrol-2,5-dione* (**6d**). According to the *G.P. B*, from **5d** [36] (1.0 g, 3 mmol): 0.40 g (52%) of **6d**. Colorless crystals. M.p. 194° (MeOH). UV: 232 (4.347). IR: 3201, 1786, 1756, 1718, 1619. ^{1}H-NMR: 11.10 (br., 1 H); 8.18 (*m*, 2 H); 7.82–7.62 (*m*, 3 H); 6.66 (*d*, *J* = 2, 1 H). ^{13}C-NMR: 170.5, 166.5, 161.8 (C=O); 149.8 (C(4)); 134.9–127.1 (arom. C); 111.9 (C(3)). Anal. calc. for $C_{11}H_7NO_4$ (217.18): C 60.83, H 3.25, N 6.45; found: C 60.96, H 3.31, N 6.41.

*3-Methoxy-1-methyl-1*H*-pyrrole-2,5-dione* (**7a**). An Et_2O soln. of diazomethane (excess) was added to a soln. of **6a** (0.13 g, 1 mmol) in MeOH (5 ml). After 4 h, the mixture was evaporated and the residue crystallized from MeOH: 0.11 g (80%) of **7a**. M.p. 130° ([17b]: M.p. 129–130°).

*3-(Benzyloxy)-1-methyl-1*H*-pyrrole-2,5-dione* (**7b**). As described for **7a**, from **6b** (0.20 g, 1 mmol) and diazomethane: 0.40 mg (60%) of **7b**. Colorless crystals. M.p. 121° (MeOH). UV: 230 (4.238). IR: 3110, 1712, 1629. ^{1}H-NMR ($CDCl_3$): 7.39 (*m*, 5 H); 5.41 (*s*, 1 H); 5.11 (*s*, 2 H); 2.99 (*s*, 3 H). Anal. calc. for $C_{12}H_{11}NO_3$ (217.22): C 66.35, H 5.10, N 6.45; found: C 66.05, H 5.21, N 6.65.

1-Benzoyl-5-methoxy-3-methyl-3-azabicyclo[3.1.0]hexane-2,4-dione (**8c**). An Et_2O soln. of diazomethane (excess) was added to a soln. of **3c** (70 mg, 0.3 mmol) in MeOH (5 ml). After the evolution of N_2 had ceased, the soln. was evaporated and the residue recrystallized from Et_2O: 25 mg (32%) of **8c**. Colorless crystals. M.p. 110°. UV: 206 (4.247), 250 (4.046). IR: 2926, 1782, 1709, 1677, 1597. ^{1}H-NMR ($CDCl_3$): 7.85–7.75 (*m*, 2 H); 7.65–7.55 (*m*, 1 H); 7.53–7.43 (*m*, 2 H); 3.63 (*s*, 3 H); 3.02 (*s*, 3 H); 2.85 (*d*, *J* = 5.5, 1 H); 2.85 (*d*, *J* = 5.5, 1 H); 2.00 (*d*, *J* = 5.5 Hz, 1 H). HR-MS. 259.0856 ($C_{14}H_{13}NO_4^+$; calc. 259.0845).

3-Benzylidene-2,3-dihydro-4-methoxy-2-methylisothiazole-5-carboxylic Acid Methyl Ester 1,1-Dioxide (**9b**). An Et_2O soln. of diazomethane (excess) was added at 0° to a stirred suspension of **9a** [18] (0.59 g, 2 mmol) in Et_2O (10 ml). As soon as a clear soln. was obtained, the mixture was evaporated: **9b** (nearly quant.). A mixture of **9a** [18] (0.59 g, 2 mmol) and tetramethyl orthocarbonate (10 ml) was refluxed for 15 min. Then the mixture was evaporated and the residue crystallized: 0.41 g (80%) of **9b**. Yellow crystals. M.p. 132° (MeOH). UV: 236 (4.918), 331 (4.218). IR: 3030, 1710, 1590, 1344, 1179. ^{1}H-NMR: 7.57–7.35 (*m*, 5 H); 6.90 (*s*, 1 H); 4.25 (*s*, MeO); 3.87 (*s*, COOMe); 2.78 (*s*, MeN). ^{13}C-NMR: 163.2 (C(4)); 158.8 (C=O); 132.4–128.6 (C(5), arom. C); 115.2 (CH=); 106.7 (C(3)); 63.9 (MeO); 52.8 (COOMe); 34.1 (MeN). MS: 309 (M^+). Anal. calc. for $C_{14}H_{15}NO_5$ (309.30): C 54.39, H 4.85, N 4.50, S 10.37; found: C 54.45, H 4.88, N 4.45, S 10.17.

*2,3-Dihydro-*4*-methoxy-3-(2-methoxy-2-oxoethylidene)-2-methylisothiazole-5-carboxylic Acid Methyl Ester 1,1-Dioxide* (**10b**) [19]. ^{13}C-NMR: 165.5, 158.6, 158.1 (C(4), C=O); 139.2 (C(5)); 108.7 (C(3)); 91.0 (CH=); 64.0 (MeO); 53.1, 51.4 (COOMe); 32.4 (MeN).

2,3-Dihydro-4-methoxy-3-oxoisothiazole-5-carboxylic Acid Methyl Ester 1,1-Dioxide (**11a**). According to the *G.P. A*, from **9a** [18] (0.59 g, 2 mmol) or **10a** [19] (0.56 g, (2 mmol): 0.25 g (57%) or 0.33 g (75%)

of **11a**, resp. Colorless crystals. M.p. 182° (Et_2O). UV: 208 (3.943), 243 (4.340). IR: 3121, 1750, 1703, 1626. ^{1}H-NMR ((D_6)DMSO/$CDCl_3$): 9.27 (*s*, 1 H); 4.45 (*s*, 3 H); 3.95 (*s*, 3 H). Anal. calc. for $C_6H_7NO_6S$ (221.18): C 32.58, H 3.19, N 6.33: found: C 32.63, H 3.28, N 6.29.

2,3-Dihydro-4-methoxy-2-methyl-3-oxoisothiazole-5-carboxylic Acid Methyl Ester 1,1-Dioxide (**11b**). According to the *G.P. A*, from **9b** (0.62 g, 2 mmol) or **10b** [19] (0.58 g, 2 mmol): 0.36 g (76%) of **11b**. Colorless crystals. M.p. 120° (Et_2O). UV: 236 (4.376), 285 (4.196). IR: 2970, 1748, 1704, 1614. ^{1}H-NMR: 4.39 (*s*, 3 H); 3.85 (*s*, 3 H); 3.04 (*s*, 3 H). ^{13}C-NMR: 165.1, 160.9, 157.5 (C(4), C=O); 111.3 (C(3)); 63.2 (MeO); 52.9 (COOMe); 23.3 (MeN). Anal. calc. for $C_7H_9NO_6S$ (235.21): C 35.75, H 3.86, N 5.96; found: C 35.77, H 3.96, N 5.93.

5-Methoxy-3-methyl-4-oxo-2-thia-3-azabicyclo[3.1.0]hexane-1-carboxylic Acid Methyl Ester 2,2-Dioxide (**12**). As described for **8c**, from **11a** (0.22 g, 1 mmol) and excessive diazomethane: 0.22 g (88%) of **12**. Colorless crystals. M.p. 95° (MeOH). UV: 210 (3.890), 234 (sh). IR: 3100, 3015, 1760, 1730. ^{1}H-NMR ($CDCl_3$): 4.02 (*s*, 3 H); 3.62 (*s*, 3 H); 3.07 (*s*, 3 H); 2.72 (*d*, *J* = 8, 1 H); 2.28 (*d*, *J* = 8, 1 H). Anal. calc. for $C_8H_{11}NO_6S$ (249.23): C 38.55, H 4.49, N 5.62; found: C 39.12, H 4.49, N 5.51.

5-Benzylidene-3-(4-methoxybenzylidene)-pyrrolidine-2,4-dione (**13b**). A soln. of 5-benzylidene-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one [26] (1.87 g, 10 mmol) in AcOH (20 ml) was heated to reflux for 10 min in the presence of ammonium acetate (1.15 g, 15 mmol) and 4-methoxybenzaldehyde (1.63 g, 12 mmol). The product crystallized after cooling: 2.0 g (65%) of **13b**, (*E*)/(*Z*) mixture 4 : 1. Orange crystals. M.p. 212° (dec.; dioxane/H_2O). UV: 307 (4.298), 381 (4.549). IR: 3186, 1718, 1664, 1634, 1583. ^{1}H-NMR (main isomer): 11.03 (*s*, 1 H); 8.77–8.57 (*m*, 2 H); 7.85–7.15 (*m*, 8 H); 6.50 (*s*, 1 H); 3.96 (*s*, 3 H). Anal. calc. for $C_{19}H_{15}NO_3$ (305.33): C 74.74, H 4.95, N 4.59; found: C 74.29, H 4.91, N 4.58.

5-Benzylidene-3-(3-phenylprop-2-enylidene]pyrrolidine-2,4-dione **(13c)**. As described for **13b**, from 5-benzylidene-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one [26] (1.87 g, 10 mmol) and cinnamaldehyde (= 3-phenylprop-2-enal; 1.60 g, 12 mmol): 1.5 g (50%) of **13c**. Red crystals. M.p. 237–239°. UV: 377 (4.669). IR: 3299, 1714, 1701, 1635. ^{1}H-NMR ((*E*)/(*Z*) 1 : 1): 11.01 (*s*, 0.5 H); 10.98 (*s*, 0.5 H); 8.35–8.23 (*m*, 1 H); 7.80–7.30 (*m*, 12 H); 6.41 (*s*, 0.5 H); 6.40 (*s*, 0.5 H). Anal. calc. for $C_{20}H_{15}NO_2$ (301.39): C 79.87, H 4.99, N 4.66; found: C 79.51, H 4.87, N 4.32.

5-Benzylidene-3-[(dimethylamino)methylene]pyrrolidine-2,4-dione (**13d**). Dimethylformamide diethyl acetal (3 ml) was added to a hot soln. of 5-benzylidene-1,5-dihydro-4-hydroxy-2*H*-pyrrol-2-one [26] (1.87 g, 10 mmol) in dioxane (20 ml). After a short time, yellowish crystals started to precipitate: 1.70 g (70%) of **13d**. M.p. 265° (dec.). UV: 315 (4.454). IR: 3300, 1702, 1676, 1633. ^{1}H-NMR: 9.95 (*s*, 1 H); 7.56–7.24 (*m*, 6 H); 6.17 (*s*, 1 H); 3.72 (*s*, 3 H); 3.36 (*s*, 3 H). ^{13}C-NMR: 179.7, 172.0 (C=O); 153.7 (N–CH=); 134.4–126.9 (C(3), C(5), arom. C); 102.8 (CH=); 47.2 (MeN). Anal. calc. for $C_{14}H_{14}N_2O_2$ (242.57): C 69.84, H 5.78, N 11.56; found: C 69.31, H 5.76, N 11.67

4-Benzylidenepyrrolidine-2,3,5-trione (**14a**). According to the *G.P. B*, from **13a** [37] (0.55 g, 2 mmol): 0.18 g (45%) of **14a**, (*E*)/(*Z*) mixture 7 : 3. Yellow crystals. M.p. 218° (dec.; MeOH). UV: 339 (4.040). IR: 3056, 1789, 1697, 1610. ^{1}H-NMR (main isomer): 12.32 (*s*, 1 H); 8.47–8.39 (*m*, 2 H); 7.87 (*s*, 1 H); 7.69–7.54 (*m*, 3 H). MS: 201 (M^+). Anal. calc. for $C_{11}H_7NO_3$ (201.18): C 65.67, H 3.51, N 6.96; found: C 64.62, H 3.63, N 6.95.

4-(4-Methoxybenzylidene)pyrrolidine-2,3,5-trione (**14b**). According to the *G.P. B*, from **13b** (0.91 g, 3 mmol): 0.48 g (70%) of **14b**, (*E*)/(*Z*) mixture 7 : 3. Yellow crystals. M.p. 215° (dec.; MeOH). UV: 252 (3.902), 387 (4.383). IR: 3259, 1779, 1745, 1690. ^{1}H-NMR (main isomer): 12.18 (*s*, 1 H); 8.60–8.47 (*m*, 2 H); 7.84 (*s*, 1 H); 7.20–7.07 (*m*, 2 H); 3.91 (*s*, 3 H). Anal. calc. for $C_7H_8N_2O_3$ (168.15): C 50.00, H 4.79, N 16.66; found: C 50.16, H 4.99, N 16.26.

4-(3-Phenylprop-2-enylidene)pyrrolidine-2,3,5-trione (**14c**). According to the *G.P. B*, from **13c** (0.60 g, 2 mmol): 0.28 g (61%) of **14c**, (*E*)/(*Z*) mixture 7 : 3. Yellow crystals. M.p. 230° (dec.; MeOH). UV: 250 (3.901), 382 (4.471). IR: 3432, 3234, 1780, 1704, 1686. ^{1}H-NMR (main isomer): 12.18 (*s*, 1 H); 8.15–8.05 (*m*, 1 H); 7.85–7.65 (*m*, 4 H); 7.55–7.45 (*m*, 3 H). Anal. calc. for $C_{13}H_9NO_3$ (227.22): C 68.72, H 3.99, N 6.16; found: C 68.52, H 4.11, N 6.07.

4-[(Dimethylamino)methylene]pyrrolidine-2,3,5-trione (**14d**). According to the *G.P. B*, from **13d** (0.97 g, 4 mmol): 0.50 g (74%) of **14d**. Colorless crystals. M.p. 253° (dec.; MeOH). UV: 277 (4.235), 336 (3.860). IR: 3129, 1770, 1731, 1673, 1636. ^{1}H-NMR: 7.58 (*s*, 1 H); 3.61 (*s*, 3 H); 3.42 (*s*, 3 H). Anal. calc. for $C_7H_8N_2O_3$ (168.15): C 50.00, H 4.79, N 16.66; found: C 50.16, H 4.99, N 16.26.

*(5Z)-2,5-Dihydro-4-methoxy-2-oxo-5-(2-oxoethylidene)-1*H*-pyrrole-3-carboxylic Acid Methyl Ester* (**17a**). According to the *G.P. B*, from **16a** [26] (1.0 g, 3.4 mmol): 0.15 g (21%) of **17a**. Yellow crystals. M.p. 80° (MeOH). From the mother liquor, **18** was obtained (see below). **17a**: UV: 297 (4.168). IR: 3197, 1720, 1673. ^{1}H-NMR ($CDCl_3$): 9.69 (*d*, *J* = 1.2, 1 H); 9.23 (br. *s*, 1 H); 6.05 (*d*, *J* = 1.2, 1 H); 4.19 (*s*, 3 H). 3.89 (*s*, 3 H). NOE: MeO–C(4) (4.19)/HC=C(5) (6.05). Anal. calc. for $C_9H_9NO_5$ (211.17): C 51.19, H 4.29, N 6.63; found: C 51.25, H 4.49, N 6.55.

*[(2Z)-1,5-Dihydro-3-methoxy-5-oxo-2*H*-pyrrol-2-ylidene]acetaldehyde* (**17b**). According to the *G.P. A*, from **16b** [26] (1.0 g, 4.5 mmol): 0.23 g (33%) of **17b**. Yellow crystals. M.p. 148° (dec.; MeOH). UV: 294 (4.211). IR: 3109, 1708, 1670, 1603. ^{1}H-NMR ($CDCl_3$): 9.67 (*d*, *J* = 1.4, 1 H); 9.07 (br., 1 H); 5.91 (*dd*, *J* = 0.4, *J* = 1.4, 1 H); 5.23 (*dd*, *J* = 0.4, 1.8, 1 H); 3.89 (*s*, 3 H). NOE: MeO–C(3) (3.89)/HC=C(2) (5.91) and H–C(4) (5.23). ^{13}C-NMR ($CDCl_3$): 190.9 (CH=O); 171.3, 167.3 (C(3), C=O); 145.5 (C(2)); 97.9 (*C*H=C(2)); 94.1 (C(4)); 60.4 (MeO). Anal. calc. for $C_7H_7NO_3$ (153.14): C 54.90, H 4.61, N 9.15; found: C 54.91, H 4.65, N 8.81.

*(5Z)-2,5-Dihydro-4-methoxy-5-(2-methoxy-2-oxoethylidene)-2-oxo-1*H*-pyrrole-3-carboxylic Acid Methyl Ester* (**18**). Compound **18** crystallized from the mother liquor obtained on preparing **17a**: 50 mg (6%) of **18**. Colorless crystals. M.p. 146° (MeOH). UV: 291 (4.296). IR: 3240, 1738, 1720, 1702, 1620. ^{1}H-NMR: 10.12 (*s*, 1 H); 5.51 (*s*, 1 H); 4.09 (*s*, 3 H); 3.81 (*s*, 3 H); 3.70 (*s*, 3 H). ^{13}C-NMR: 166.9, 165.1 (C=O); 163.2 (C(4)); 162.1 (C=O); 143.7 (C(5)); 100.9 (CH=); 93.8 (C(3)); 61.2 (MeO); 52.4 (COO*Me*); 51.5 (COO*Me*). Anal. calc. for $C_{10}H_{11}NO_6$ (241.20): C 49.79, H 4.56, N 5.80; found: C 49.59, H 4.67, N 5.77.

*Bromo[(2Z)-1,5-dihydro-3-methoxy-5-oxo-2*H*-pyrrol-2-ylidene]acetaldehyde* (**19b**). Five drops of Br_2 were added to a suspension of **17b** (0.15 g, 1 mmol) in AcOH (3 ml). After a short time of stirring, the product began to crystallize. The precipitate was collected and washed with petroleum ether: 80 mg (35%) of **19b**.Yellowish crystals. M.p. 260° (dec.; MeOH). UV: 308 (4.289). IR: 3176, 3113, 1705, 1660, 1593. ^{1}H-NMR: 10.41 (br. *s*, 1 H); 9.52 (*s*, 1 H); 5.79 (*s*, 1 H); 3.95 (*s*, 3 H). NOE: MeO–C(3) (3.95)/H–C=O (9.52) and H–C(4) (5.79). Anal. calc. for $C_7H_6BrNO_3$ (232.03): C 36.24, H 2.61, N 6.04; found: C 36.07, H 2.47, N 5.94.

*Bromo[4-bromo-1,5-dihydro-3-methoxy-5-oxo-2*H*-pyrrolylidene]acetaldehyde* (**19c**). Ten drops of Br_2 were added to a soln. of **17b** (0.15 g, 1 mmol) in AcOH (15 ml). After 30 min of stirring, the mixture was evaporated and the residue crystallized from ^{i}Pr$_2$O/EtOH (1:1): 70 mg (22%) of **19c**. Yellowish crystals. M.p. 207° (dec.; AcOH). UV: 319 (4.376). IR: 3155, 1718, 1664, 1591. ^{1}H-NMR: 10.87 (*s*, 1 H); 9.96 (*s*, 1 H); 4.34 (*s*, 3 H). Anal. calc. for $C_7H_5Br_2NO_3$ (310.93): C 27.04, H 1.62, N 4.50; found: C 27.14, H 1.87, N 4.42.

*4-Amino-2,5-dihydro-2-oxo-5-(2-oxoethylidene)-1*H*-pyrrole-3-carboxylic Acd Methyl Ester* (**20**). A soln. of NH_3 (1 ml, 25%) was added to a soln. of **17a** (0.11 g, 0.5 mmol) in MeOH (5 ml). After a short time of stirring, the product began to crystallize: 80 mg (81%) of **20**. Colorless crystals. M.p. 193° (dec.; MeOH). UV: 230 (4.014), 314 (4.145). IR: 3398, 1719, 1638, 1560. ^{1}H-NMR: 10.66 (*s*, 1 H); 9.97 (*d*, *J* = 8, 1 H); 8.71 (br. *s*, 1 H); 8.21 (br. *s*, 1 H); 6.14 (*d*, *J* = 8, 1 H); 3.68 (*s*, 3 H). MS-HR: 196.0522 ($C_8H_8N_2O_4^+$; calc. 196.0484).

rel-(*3a*R,*3b*R,*6a*S,*6b*S)*-Tetrahydro-3a,3b-dimethoxy-2,5-dimethylcyclobuta[1,2-*c*:3,4-*c′*]dipyrrole-1,3,4,6(2*H,*5*H*)-tetrone* (**22a**). A soln. of **7a** (0.12 g, 0.8 mmol) in $CHCl_3$ (100 ml) was irradiated for 2 h and then evaporated. The residue was recrystallized: 0.11 g (90%) of **22a**. Colorless crystals. M.p. 215° (EtOH/^{i}Pr$_2$O). The structure was confirmed by X-ray crystallography[1]). UV: 260 (2.756). IR: 2953, 1780, 1721. ^{1}H-NMR ($CDCl_3$): 3.45 (*s*, 6 H); 3.12 (*s*, 6 H); 3.09 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 172.5 (C=O); 83.5 (C–O); 55.1 (MeO); 40.8 (C–H); 25.6 (MeN). MS: 286 (M^+). Anal. calc. for $C_{12}H_{14}N_2O_6$ (282.26): C 51.07, H 5.00, N 9.92; found: C 50.92, H 5.05, N 9.79.

rel-(*3a*R,*3b*R,*6a*S,*6b*S)*-3a,3b-Bis(benzyloxy)-tetrahydro-2,5-dimethylcyclobuta[1,2-*c*:3,4-*c′*]dipyrrole-1,3,4,6(2*H,*5*H*)-tetrone* (**22b**). As described for **22a**, from **7b** (0.11 g, 0.5 mmol): 50 mg (45%) of **22b**. Colorless crystals. M.p. 143° (MeOH). The structure was confirmed by X-ray crystallography[1]). UV: 210 (4.409). IR: 3473, 1778, 1799. ^{1}H-NMR: 7.40–7.19 (*m*, 10 H); 4.64 (*d*, *J* = 11.3, 4 H); 3.63 (*d*, *J* = 4, 2 H); 2.98 (*s*, 6 H). ^{13}C-NMR : 172.9, 170.7 (C=O); 136.6–127.2 (arom. C); 82.9 (C–O); 67.8 (CH_2–O); 25.1 (MeN). Anal. calc. for $C_{24}H_{22}N_2O_6$ (434.45): C 66.35, H 5.10, N 6.45; found: C 66.08, H 5.09, N 6.25.

rel-(*3a*R,*3b*R,*6a*S,*6b*S)*-3a,3b,6a,6b-Tetrakis(benzyloxy)tetrahydro-2,5-dimethylcyclobuta[1,2-*c:*3,4-c′]dipyrrole-1,3,4,6(2*H,*5H)-tetrone* (**22c**). A soln. of **23a** [34] (0.32 g, 1 mmol) and benzophenone (0.1 g) in AcOEt/hexane 1:10 (150 ml) was irradiated for 1.5 h. After concentration of the soln. to $^1/_{10}$ of the original volume, the product precipitated upon cooling: 0.21 g (65% of **22c**). Colorless powder. M.p. 196°. IR: 3088, 3065, 2942, 2883, 1782, 1721, 1610. ^{1}H-NMR ($CDCl_3$): 7.26–7.20 (*m*, 20 H); 5.04 (*d*, *J* = 10.6, 4 H); 4.98 (*d*, *J* = 10.6, 4 H); 3.06 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 170.9 (C=O); 136.6–127.8 (arom. C); 81.4 (C–O); 70.5 (CH_2–O); 23.2 (MeN). MS: 646 (M^+). Anal. calc. for $C_{38}H_{34}N_2O_8$ (646.70): C 70.58, H 5.30, N 4.33; found: C 70.54, H 5.29, N 4.38.

*3-(*tert*-Butoxy)-4-methoxy-1-methyl-1*H*-pyrrole-2,5-dione* (**23b**). An Et_2O soln. of diazomethane (excess) was added to the soln. of 3-(*tert*-butoxy)-4-methoxy-1*H*-pyrrole-2,5-dione [38] (0.4 g, 2 mmol) in MeOH (10 ml). After the evolution of N_2 had ceased, the soln. was evaporated and the residue purified by CC (petroleum ether). The initially oily substance crystallized slowly: 0.27 g (63%) of **23b**. Yellow crystals. M.p. 35°. UV: 234 (4.127). IR: 2981, 1778, 1724, 1673. ^{1}H-NMR ($CDCl_3$): 4.11 (*s*, 3 H); 2.95 (*s*, 3 H); 1.44 (*s*, 9 H). Anal. calc. for $C_{10}H_{15}NO_4$ (213.24): C 56.33, H 7.09, N 6.57, found: C 56.36, H 7.07, N 6.91.

rel-(*3a*R,*3b*S,*6a*R,*6b*S)*-3a,3b,6a,6b-Tetrakis(benzyloxy)-tetrahydro-2,5-dimethylcyclobuta[1,2-*c:*3,4-c′]dipyrrole-1,3,4,6(2*H,*5H)-tetrone* (**24a**). As described for **22a**, from **23a** [34] (0.32 g, 1 mmol) by irradiation for 6 h: 0.28 g (43%) of **24a**. Colorless crystals. M.p. 129° (AcOEt/hexane). The structure was confirmed by X-ray crystallography[1]). IR: 3059, 3030, 2890, 1783, 1726. ^{1}H-NMR ($CDCl_3$): 7.51–7.24 (*m*, 20 H); 5.02 (*d*, *J* = 10.2, 4 H); 4.97 (*d*, *J* = 10.2, 4 H); 3.05 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 170.8 (C=O); 136.6–127.9 (arom. C); 80.5 (C–O); 70.42 (CH_2–O); 25.14 (MeN). MS: 465 ($[M - C_{14}H_{14}]^+$). Anal. calc. for $C_{38}H_{34}N_2O_8$ (646.70): C 70.58, H 5.30, N 4.33; found: C 70.54, H 5.29, N 4.38.

rel-(*3a*R,*3b*S,*6a*R,*6b*S)*-3a,6a-Di(*tert*-butoxy)-tetrahydro-3b,6b-dimethoxy-2,5-dimethylcyclobuta[1,2-*c:*3,4-c′]dipyrrole-1,3,4,6(2*H,*5H)-tetrone* (**24b**). As described for **22a**, from **23b** (0.11 g, 0.5 mmol): 35 mg (32%) of **24b**. Colorless crystals. M.p. 175° (MeOH). The structure was confirmed by X-ray crystallography[1]). UV: 207 (4.222). IR: 2976, 2953, 1778, 1731. ^{1}H-NMR: 3.80 (*s*, 6 H); 2.89 (*s*, 6 H); 1.37 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$): 172.9, 170.8 (C=O); 80.0 (quart. C); 56.8 (MeO, C–O); 29.2 (Me_3C); 25.1 (MeN). Anal. calc. for $C_{20}H_{30}N_2O_8$ (426.46): C 56.33, H 7.09, N 6.57; found: C 56.09, H 6.98, N 6.54.

rel-(*3a*R,*3b*S,*6a*R,*6b*S)*-Tetrahydro-3a,3b,6a,6b-tetrahydroxy-2,5-dimethylcyclobuta[1,2-*c:*3,4-c′]-dipyrrole-1,3,4,6(2*H,*5H)-tetrone* (**24c**). A suspension of **24a** (0.39 g, 0.6 mmol) and 10% Pd/C (50 mg) in MeOH (50 ml) was stirred at r.t. for 18 h under H_2 (1 bar). The mixture was filtered through 'Kieselguhr' (diatomaceous earth), and the filtrate was evaporated: 0.15 g (95%) of **24c**. Colorless powder. M.p. 187°. IR: 3417, 3317, 2961, 1774. ^{1}H-NMR: 6.93 (*s*, 4 OH); 2.78 (*s*, 6 H). MS: 286 (M^+). Anal. calc. for $C_{10}H_{10}N_2O_8$ (286.20): C 41.97, H 3.52, N 9.79; found: C 41.99, H 3.58, N 9.63.

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