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Linear and Cyclic *N*-Acyl-α-arylglycines. IV [1]

### Novel 3-Substituted 3-Acylaminobenzo[*b*]furan-2(3*H*)-ones: Synthesis and Chemiluminescence Studies

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Abstract. Starting from 3-acylaminobenzo[b]furan-2(3H)ones (2) 3-arylthio substituted derivatives (3) were prepared *via* novel *N*-acylimines (5). Compounds of type 3 and 5 were found to show visible chemiluminescence upon base-induced oxidation in the presence of an oxygen source. A mechanistic interpretation for this chemiluminescence reaction is proposed.

Chemiluminescence (cl) can be defined as the emission of light as a result of generation of electronically excited states of reaction products. This occurs at temperatures below those necessary for incandescence [2]. Whereas most of the chemiluminescence reactions are weak there is enormous effort to find efficient chemiluminescence compounds for using in medicinal diagnostics and analytical chemistry.

Recently, we have reported on the synthesis of a series of novel chemiluminescence compounds characterised by a linear or cyclic *N*-acyl- $\alpha$ -arylglycine substructure (1, 2) [1,3]. Moreover, the cl measurement of 3-acylaminobenzo[*b*]furan-2(3*H*)-ones (2, 3) has been described [3] and the utility of this system for application as diagnostics has been demonstrated [4].



Here, we report on the synthesis of 3-acylaminobenzo[b]furan-2(3H)-ones of type **3**, bearing an aryl(alkyl)thio or an arylsulfonyl substituent in position 3. Moreover, chemiluminescence studies as well as a postulated mechanism for the cl reaction are presented.

### **Results and Discussion**

The target compounds 3a - e were synthesised as outlined in Scheme 1. The 3-acylaminobenzo[b]furan-2(3H)-ones (2a-d) could be easily prepared by acid induced electrophilic  $\alpha$ -amidoalkylation of substituted phenols and subsequent cyclisation or reduction and N-acetylation of benzo[b]furan-2,3-dione 3-oxime (4) [5], respectively. The novel N-acylimines 5a-d then became accessible by treatment of 2a - d with 3 equivalents of N-bromosuccinimide (NBS) and catalytic amounts of  $\alpha$ ,  $\alpha$ '-azoisobutyronitrile (AIBN) in dry tetrachloromethane (in analogy to a previously reported method [6]). However, employment of the acetamide derivatives  $2\mathbf{a} - \mathbf{c}$  (compounds of type 2 with  $\mathbf{R}^1 = \mathbf{CH}_3$ ) resulted in the formation of N-acylimines containing traces of the corresponding bromomethyl derivatives. Attempts to purify compounds 5a-c by column chromatography resulted in degradation of the compounds. Characterisation of 5a-d was performed by IR and <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectra of the *N*-acylimines (5a-d) are characterised by the absence of the NH and H-3 signals whereas the IR spectra show a C=N bond at 1660–1685 cm<sup>-1</sup>. The methyl urethane derived *N*-acylimine 5d could be recrystallised from ethyl acetate/light petroleum to give an analytically pure compound.

Reaction of the *N*-acylimines  $(5\mathbf{a}-\mathbf{d})$  with *S*-nucleophiles (4-chlorothiophenol, benzylmercaptane, or 4toluenesulfinic acid, respectively) in tetrahydrofuran with catalytic amounts of base (triethylamine) gave the target compounds  $3\mathbf{a}-\mathbf{e}$  in good to moderate yields. Using one equivalent of base, however, led to the formation of the corresponding dimeric products **6** [7]. aminobenzo[b]furanones bearing a hydrogen atom in position 3. Whereas compounds of type 1 and 2 exhibit long continuous emission of light (minutes to hours), the N-acylimines (5a-d) and the derivatives bearing RS in position 3 (3a-e) display a flash and then after addition of hydrogen peroxide emit continuous light (minutes). From these observations, we suggest that compounds of type 3 and 5 exhibit their cl properties by a different mechanism compared to compounds 1 and 2 (for the mechanism of the latter compounds see [3]). The first step in this suggested mechanism is the formation of an N-acylimine (5) [8] which upon contact with air emits a flash of light. Addition of hydrogen peroxide leads to the hydroperoxide anion 7. Furthermore, the hydroperoxide anion function undergoes an intramolecular reaction with the lactone part of the



### Scheme 1

Visible chemiluminescence of the novel compounds of type **3** and **5** can be observed upon treatment with base (preferably 1,8-diazabicyclo[5.4.0]undec-7-ene) in polar aprotic solvents (*e.g.* acetone) in the presence of air or oxygen. The process of light emission, however, seems different from that of the corresponding 3-acyl-

molecule to give the dioxetanone 8. Loss of carbon dioxide leads to 9 in an electronically excited state which then emits continuous light until reaching the ground state.

A proof for the mechanism described above is the isolation of the 4-toluenesulfinic acid derivative 11



which is obtained by treating the products of the chemiluminescence reaction of **3e** with the mannich base **10** [9] (see Scheme 3).





The explanation given in Scheme 2 coupled with the evidence shown in Scheme 3 leads to the confirmation that compounds of type **3** are bearing an anionic leaving group ( $RSO_2^-$ ). By contrast, compounds of type **1** and **2** possess a cationic leaving group ( $H^+$ , [3]). Accordingly, derivatives without leaving group in position 3 (3-acylamino-3-alkylbenzo[*b*]furan-2(3*H*)ones [10]) do not show visible chemiluminescence.

As shown in Tab. 1, 3-acylaminobenzo[b]furan-2(3H)-ones bearing a 3-(4-methylphenylsulfonyl) substituent (3d, 3e) show stronger chemiluminescence than derivatives with 3-(4-chlorophenylthio) (3a) or 3-benzylthio (3b, 3c) residue. This is due to the fact that sulfones with electron withdrawing substituents in  $\alpha$ -position eliminate sulfinic acid in basic medium under mild conditions [11, 12]. In contrast to the chemiluminescence of compounds of type 1 and 2, derivatives of type 3 possess the advantage that peroxidase (POD) is not required for the reaction. This can be interpreted with the mechanism described above as well as with the mechanism proposed for the chemiluminescence reaction with POD (transformation of compounds of type 1 and 2 into the corresponding N-acylimines [4]).

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### **Experimental**

Melting points were determined with a Linström apparatus and are uncorrected. IR spectra were taken on a Pye Unicam SP 3-200S spectrophotometer (KBr pellets). <sup>1</sup>H NMR spectra were recorded on a Varian EM 360 (60 MHz; TMS as internal standard,  $\delta$ -values in ppm). Reactions were monitored by TLC using Polygram<sup>®</sup> SIL G/UV<sub>254</sub> (Macherey–Nagel) plasticbacked plates (0.25 mm layer thickness). Microanalyses were performed at the Institute of Organic Chemistry and Biochemistry, University of Hamburg (Germany) and Institute of Physical Chemistry (Mag. J. Theiner), University of Vienna (Austria). Light petroleum refers to the fraction of *b.p.* 40– 60 °C. The yields are not optimised.

Chemiluminescence measurements were performed with a Biolumat LB 9500C (Berthold).

**Care:** the brominated derivatives are very irritant! The 3-acetylaminobenzo[*b*]furan-2(3*H*)ones (**2a** and **2c**) were prepared as described in [3]. The benzo[*b*]furan-2,3-dione 3oxime (**4**) became available as reported [5].

### 3-Acetylaminobenzo[b]furan-2(3H)one (2b) [13]

9 mmol of benzo[b]furan-2,3-dione-3-oxime (4 [5]) were dissolved in a mixture of 3 ml of acetic anhydride and 7 ml of acetic acid. The reaction mixture was stirred at 40-50 °C, and 36 mmol of Zn were added during 1 h, then the mixture was stirred for additional 15 min. at 50 °C. After cooling to room temperature, the precipitate was filtered off, and the solvent was removed in vacuo. The product thus obtained was recrystallised from tetrahydrofuran/light petroleum to yield 71% of colourless crystals, m.p. 180-180 °C (no data are given in [13]). - IR: v/cm<sup>-1</sup> = 3300 (NH), 1835 (lactone-C=O), 1650 (NC=O).  $- {}^{1}$ H NMR (DMSO-d<sub>6</sub>):  $\delta$ /ppm = 9.14 (d, 1H, D<sub>2</sub>O-exchangeable), 7.56-7.01 (m, 4H, phenyl-H), 5.38 (d, 1H, D<sub>2</sub>O-exchangeable), 1.90 (s, 3H, CH<sub>3</sub>).  $C_{10}H_0NO_3$ Calcd.: C 62.82 H 4.74 N 7.33 (191.19)C 62.83 H 4.79 N 7.25. Found:

# 5-Chloro-3-methoxycarbonylaminobenzo[b]furan-2(3H)one (2d)

10 mmol (0.921 g) of glyoxylic acid monohydrate, 10 mmol (0.751 g) of methylcarbamate and 10 mmol (1.286 g) of p-chlorophenol were dissolved in a mixture of 10 ml of formic

| No.                                    | $\mathbb{R}^1$   | R <sup>2</sup>   | Colour and intensity of the emitted light <sup>a</sup> ) | chemiluminescence <sup>b</sup> )<br>counts (quantity <sup>c</sup> )) |                                                     | <br> |
|----------------------------------------|------------------|------------------|----------------------------------------------------------|----------------------------------------------------------------------|-----------------------------------------------------|------|
| 3a <sup>d</sup> )<br>3b <sup>d</sup> ) | $CH_3$<br>$CH_3$ | $CH_3$<br>$CH_3$ | greenish (weak)<br>greenish (weak)                       |                                                                      |                                                     |      |
| 3c                                     | CH <sub>3</sub>  | Н                | greenish (weak)                                          | 969                                                                  | (10 nmol)                                           |      |
| 3d                                     | CH <sub>3</sub>  | Cl               | greenish (very strong)                                   | 919,645<br>536,459                                                   | (10 nmol)<br>(1 nmol)                               |      |
| 3e                                     | OCH <sub>3</sub> | Cl               | greenish (very strong)                                   | > 999,999<br>878,213<br>without POD<br>> 999,999<br>858,216          | (10 nmol)<br>(1 nmol)<br>:<br>(10 nmol)<br>(1 nmol) |      |

Tab. 1 Chemiluminescence Data of 3-Substituted 3-Acylaminobenzo[b]furan-2(3H)-ones 3a-e.

a) based on observation (reaction in acetone with 1,8-diazabicyclo[5.4.0]undec-7-ene, air oxygen, and hydrogen peroxide).

<sup>b</sup>) based on measurement (reaction in acetonitrile and phosphate buffer (pH 7.8) with peroxidase and hydrogen peroxide) [4]

<sup>c</sup>) total quantity of the chemiluminescent compound in the reaction mixture

d) contains the 0.2 - 0.3 molequiv. of the corresponding bromo derivative.

acid containing 5 drops of conc. sulphuric acid, and the mixture was stirred at room temperature for 3 days. The residue obtained after removal of the formic acid was dissolved in 50 ml of ethyl acetate, and the organic layer was washed with water  $(3 \times 20 \text{ ml})$ , dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo*. The residue was recrystallised from tetrahydrofuran/light petroleum to yield 70% of colourless crystals, *m.p.* 191–193 °C. – IR: v/cm<sup>-1</sup> = 3380 (NH), 1805 (lactone-C=O), 1705 (NC=O). – <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\partial/$ ppm = 8.33 (d, 1H, D<sub>2</sub>O-exchangeable), 7.49–7.13 (m, 3H, phenyl-H), 5.36 (d, 1H, D<sub>2</sub>O-exchangeable), 3.54 (s, 3H, CH<sub>3</sub>).

#### Synthesis of the *N*-Acylimines (5a–d) (General Procedure)

To a suspension of 15 mmol of 3-acylaminobenzo[b]furan-2(3H)one (2a-d) and 45 mmol of N-bromosuccinimide in 60 ml of dry tetrachloromethane was added a catalytic amount of  $\alpha, \alpha'$ -azoisobutyronitrile, and the mixture was refluxed until the starting material was completely consumed. The reaction mixture was cooled to room temperature, filtered under a dry nitrogen atmosphere, and the solvent was removed *in vacuo*. To the residue were added 20 ml of dry ethyl acetate, and the solvent was removed was treated with 10 ml of dry diethyl ether, the crystals were collected and washed with dry light petroleum and dry diethyl ether.

### 3-Acetylimino-5-methylbenzo[b]furan-2(3H)one (5a)

Reaction time: 3 h. Recrystallisation from cyclohexane afforded yellow crystals (yield 59%), *m.p.* 97–99 °C. – IR:  $\nu/cm^{-1} = 1820$  (lactone-C=O), 1720 (NC=O), 1685 (C=N). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta/ppm = 7.85-6.61$  (m, 3H, phenyl-H), 4.49 (s, traces, CH<sub>2</sub>Br), 2.22 (s, 3H, CH<sub>3</sub>), 2.07 (s, 3H, CH<sub>3</sub>). C<sub>11</sub>H<sub>9</sub>NO<sub>3</sub>·0.1 C<sub>11</sub>H<sub>8</sub>BrNO<sub>3</sub> (231.41) Calcd.: C 62.80 H 4.27 N 6.66

| 31.41) | Calcd.: | C 62.80 | H 4.27 | N 6.66 |
|--------|---------|---------|--------|--------|
|        | Found : | C 62.73 | H 4.55 | N 6.33 |

### 3-Acetyliminobenzo[b]furan-2(3H)one (5b)

Reaction time: 3 h. Recrystallisation from ethyl acetate/light petroleum afforded yellow crystals (yield 69%), *m.p.* 95–98

°C. – IR:  $\nu/cm^{-1}$  = 1810 (lactone-C=O), 1715/1710 (NC=O), 1670 (C=N). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ /ppm = 7.85–7.13 (m, 4H, phenyl-H), 2.44 (s, 3H, CH<sub>3</sub>). C<sub>10</sub>H<sub>7</sub>NO<sub>3</sub>·0.03 C<sub>10</sub>H<sub>6</sub>BrNO<sub>3</sub> (197.21) Calcd.: C 62.73 H 3.67 N 7.32 Found: C 62.73 H 3.65 N 7.33.

3-Acetylimino-5-chlorobenzo[b]furan-2(3H)one (5c)

Reaction time: 1 h 45 min. Recrystallisation from ethyl acetate/ light petroleum afforded yellow crystals (yield 56%), *m.p.* 105–109 °C. – IR: v/cm<sup>-1</sup> = 1820 (lactone-C=O), 1715/1690 (NC=O), 1660 (C=N). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ /ppm = 7.66–7.10 (m, 3H, phenyl-H), 4.21 (s, traces, CH<sub>2</sub>Br), 2.40 (s, 3H, CH<sub>3</sub>).

 $\begin{array}{c} C_{10}H_6CINO_3 \cdot 0.1 \ C_{10}H_5BrCINO_3 \\ (251.52) \quad Calcd.: \ C \ 53.01 \quad H \ 2.60 \quad N \ 6.13 \\ Found: \ C \ 53.09 \quad H \ 2.65 \quad N \ 5.88. \end{array}$ 

5-Chloro-3-methoxycarbonyliminobenzo[b]furan-2(3H)one (5d)

Reaction time: 47 h. Recrystallisation from ethyl acetate/light petroleum afforded yellow crystals (yield 84%), *m.p.* 126–128 °C. – IR:  $\nu/cm^{-1}$  = 1820 (lactone-C=O), 1740 (NC=O), 1665 (C=N). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ /ppm = 7.75–7.13 (m, 3H, phenyl-H), 4.01 (s, 3H, CH<sub>3</sub>).

 $\begin{array}{cccc} C_{10}H_6CINO_4 & Calcd.: C \ 50.13 & H \ 2.52 & N \ 5.85 & Cl \ 14.80 \\ (239.62) & Found: C \ 49.95 & H \ 2.63 & N \ 5.87 & Cl \ 14.56. \end{array}$ 

## Synthesis of 3,3-Disubstituted Benzo[*b*]furan-2(3*H*)-ones (3a-e) (General Procedure)

To a solution of 5 mmol of the *N*-acylimine (5a-d) in 10 ml of dry tetrahydrofuran was added dropwise a solution of 5 mmol of the corresponding *S*-nucleophile and 3 drops of triethylamine in 10 ml of tetrahydrofuran. The reaction mixture was stirred overnight at room temperature.

### 3-Acetylamino-3-(4-chlorophenylthio)-5-methylbenzo[b]furan-2(3H)one (**3a**)

The solvent was removed *in vacuo*, and the oily residue thus obtained was crystallised with diethyl ether. Recrystallisation from ethyl acetate  $(3\times)$  afforded colourless crystals (yield

69%), *m.p.* 170–171 °C (dec.). – IR:  $\nu$ /cm<sup>-1</sup> = 3250 (NH), 1810 (lactone-C=O), 1655 (NC=O). – <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$ /ppm = 9.83, 9.72 (s, 1H, D<sub>2</sub>O-exchangeable, NH), 7.65– 6.86 (m, 7H, phenyl-H), 4.71 (s, traces, CH<sub>2</sub>Br), 2.26 (s, nearly 3H, CH<sub>3</sub>), 1.90 (s, 3H, CH<sub>3</sub>). C<sub>17</sub>H<sub>14</sub>ClNO<sub>3</sub>S · 0.3 C<sub>17</sub>H<sub>13</sub>BrClNO<sub>3</sub>S (475.84) Calcd.: C 55.78 H 3.79 N 3.83

Found: C 55.98 H 3.94 N 3.69.

3-Acetylamino-3-benzylthio-5-methylbenzo[b]furan-2(3H)one (**3b**)

The solvent was removed *in vacuo*, and the oily residue thus obtained was crystallised with light petroleum. Recrystallisation from ethyl acetate/light petroleum (3×) afforded colourless crystals (yield 61%), *m.p.* 150 °C. – IR: *v/*cm<sup>-1</sup> = 3250 (NH), 1815 (lactone-C=O), 1660 (NC=O). – <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\partial/$ ppm = 9.68 (s, 1H, D<sub>2</sub>O-exchangeable, NH), 7.48–7.01 (m, 8H, phenyl-H), 4.74 (s, traces, CH<sub>2</sub>Br), 4.16 (s, 2H, CH<sub>2</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 1.94 (s, 3H, CH<sub>3</sub>). C<sub>18</sub>H<sub>17</sub>NO<sub>3</sub>S · 0.2 C<sub>18</sub>H<sub>16</sub>BrNO<sub>3</sub>S (408.67) Calcd.: C 63.48 H 4.98 N 4.11 S 9.42 Found: C 63.20 H 4.70 N 4.02 S 9.43.

### 3-Acetylamino-3-benzylthiobenzo[b]furan-2(3H)one (3c)

The solvent was removed *in vacuo* and the oily residue thus obtained was crystallised with diethyl ether. Recrystallisation from tetrahydrofuran/light petroleum afforded light yellow crystals (yield 80%), *m.p.* 163–164 °C (dec.). – IR: *v/*cm<sup>-1</sup> = 3240 (NH), 1810 (lactone-C=O), 1650 (NC=O). – <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$ /ppm = 9.69 (s, 1H, D<sub>2</sub>O-exchangeable, NH), 7.46–7.06 (m, 9H, phenyl-H), 4.17 (s, 2H, CH<sub>2</sub>), 1.93 (s, 3H, CH<sub>3</sub>).

 $\begin{array}{c} C_{17}H_{15}NO_3S \quad Calcd.: C\ 65.16 \quad H\ 4.82 \quad N\ 4.47 \quad S\ 10.23 \\ (313.38) \quad \qquad Found: C\ 65.22 \quad H\ 4.98 \quad N\ 4.47 \quad S\ 10.28. \end{array}$ 

### 3-Acetylamino-5-chloro-3-(4-methylphenylsulfonyl)benzo[b]furan-2(3H)one (**3d**)

The solvent was removed *in vacuo* and the oily residue thus obtained was washed three times with light petroleum, and crystallised with acetone/diethyl ether. Recrystallisation from tetrahydrofuran/light petroleum afforded light yellow crystals (yield 81%), *m.p.* 159 °C (dec.). – IR: *v*/cm<sup>-1</sup> = 3310 (NH), 1820 (lactone-C=O), 1660 (NC=O), 1340, 1155 (SO<sub>2</sub>). – <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$ /ppm = 10.03 (s, 1H, D<sub>2</sub>O-exchangeable, NH), 7.90–7.28 (m, 7H, phenyl-H), 2.47 (s, 3H, CH<sub>3</sub>), 1.97 (s, 3H, CH<sub>3</sub>).

C<sub>17</sub>H<sub>14</sub>CINO<sub>5</sub>S

(379.82) Calcd.: C 53.76 H 3.72 N 3.69 Cl 9.33 S 8.44 Found: C 53.72 H 3.62 N 3.71 Cl 9.41 S 8.59.

### 5-Chloro-3-methoxycarbonylamino-3-(4-methylphenylsulfonyl)-benzo[b]furan-2(3H)one (3e)

The resulting crystals were collected and washed with diethyl ether. The oily residue obtained after removing the solvent was crystallised with diethyl ether/light petroleum. Recrystallisation from ethyl acetate/light petroleum afforded light yellow crystals (yield 72%), *m.p.* 169–170 °C. – IR: *v*/cm<sup>-1</sup> = 3310 (NH), 1810 (lactone-C=O), 1730 (NC=O), 1340, 1150 (SO<sub>2</sub>). – <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$ /ppm = 9.60 (s, 1H, D<sub>2</sub>O-exchangeable, NH), 7.88–7.04 (m, 7H, phenyl-H), 2.46 (s, 3H, CH<sub>3</sub>), 1.18 (s, 3H, CH<sub>3</sub>).

 $C_{17}H_{14}CINO_6S$ 

(395.82) Calcd.: C 51.59 H 3.57 N 3.54 Cl 8.96 S 8.10 Found: C 51.21 H 3.70 N 3.71 Cl 8.98 S 7.98.

### Reagents and Solutions for Chemiluminescence Measurements

Peroxidase (ca. 250 U/mg) Boehringer Mannheim, No. 413 470.

*Phosphate buffer I* (pH 7.8): 13.6 g  $KH_2PO_4$  were dissolved in aqua bidest., 8N NaOH was added until pH 7.8, and the solution was filled up with aqua bidest. to 100.0 ml.

*Phosphate buffer II* (pH 7.8): dilution of phosphate buffer I and aqua bidest. (1:100).

*EDTA solution*: 37.1 mg of EDTA disodium salt dihydrate were dissolved in 100 ml of aqua bidest., the pH was brought up to 7.0 by slow addition of 1N NaOH.

*POD solution* (2500 U/l): 1 mg of peroxidase lyophilisate were dissolved in 2.0 ml of phosphate buffer II, and this solution was diluted 1:50 with phosphate buffer II.

 $H_2O_2$  solution (ca. 1 mmolar): 10 µl conc.  $H_2O_2$ -solution were diluted with 100.0 ml of aqua bidest.

Solutions of the chemiluminescent substance in acetonitrile: a) (10 mmol/l): 0.05 mmol of the chemiluminescent substance were dissolved in 5.0 ml of acetonitrile.

b) (100 µmol/l): Solution a) was diluted 1:100 with acetonitrile. c) (10 µmol/l): Solution a) was diluted 1:1000 with acetonitrile.

#### Measurement of Chemiluminescence

In a cuvette were pipetted 200  $\mu$ l of phosphate buffer I, 200  $\mu$ l of EDTA solution (and 100  $\mu$ l of POD solution). After addition of 100  $\mu$ l of the solution of chemiluminescent compound, 200  $\mu$ l of H<sub>2</sub>O<sub>2</sub> solution were injected and the maximum (mode of measurement: 'rate') was read.

### **Observation of Chemiluminescence**

A few mg of the benzofuranone were dissoved in acetone and some drops of DBU were added ( $\rightarrow$  flash). Then, some drops of conc. hydrogen peroxide were added, and colour and intensity of the emitted light was observed in a dark room.

### Isolation of the Chemiluminescence Reaction Product 4-Toluenesulfinic Acid as Sulfone

To a solution of 2 mmol of 5-chloro-3-methoxycarbonylamino-3-(4-methylphenylsulfonyl)-benzo[*b*]furan-2(3*H*)one (**3e**) in 10 ml of acetone were added 2 mmol of DBU, and the mixture was stirred at room temperature for 30 mins. Then the solvent was removed *in vacuo*, and the residue thus obtained was treated with 7 ml of water. After filtration, 2 mmol of 3-dimethylamino-1-phenylpropan-1-one • HCl [9] were added to the filtrate, and the mixture was heated to 100 °C. After cooling to room temperature, the resulting crystals were collected, washed with water and dried. *m.p.* 135–137 °C ([14]: *m.p.* 136 °C).

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[1] for part III see: B. Matuszczak, Monatsh. Chem. 128 (1997) 945

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