Functionalized 1,2-Dioxetanes as Potential Photogenotoxic Agents: 1,2-Dioxetanes with Electrophilic Chemical Handles for the Functionalization with Protic Nucleophiles

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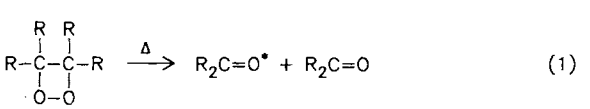
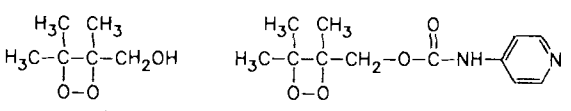
The electrophilically substituted 3-[(chlorocarbonyloxy)methyl]- and 3-{[(chlorosulfonyl)carbamoyloxy]methyl}-3,4,4-trimethyl-1,2-dioxetanes **2** and **3**, derived from 3-(hydroxymethyl)-3,4,4-trimethyl-1,2-dioxetane (**1**), are convenient substrates for the functionalization with protic nucleophiles. For example, with methanol, lauryl alcohol, and cholesterol the dioxetanes **4a–c** and with phenol and thiophenol **4d** and **4e** were prepared. With acetone oxime and benzaldoxime under base catalysis the dioxetanes **5a** and **5b** were obtained. The bis-dioxetanes **6a** and **6b** were made available in good yields by treatment of **2** with ethylenediamine and hydrazine, respectively. Glycine and its ethyl ester gave the dioxetanes **7a, b**, while ethyl phenylalanate afforded **7c**. The dipeptide-substituted dioxetane **7d** resulted from L-phenylalanyl-L-leucine, while aniline and **3** led to 3,3,4-trimethyl-4-{[(phenylsulfamoyl)carbamoyloxy]methyl}-1,2-dioxetane (**8**). By means of this synthetic methodology a variety of functionalized dioxetanes has been made available for photobiological exploration as photogenotoxic agents.

Funktionalisierte 1,2-Dioxetane als potentielle photogentoxische Agentien: 1,2-Dioxetane mit elektrophilen chemischen Handgriffen für die Funktionalisierung mit protischen Nucleophilen

Die elektrophil substituierten 3-[(Chlorcarbonyloxy)methyl]- und 3-{[(Chlorsulfonyl)carbamoyloxy]methyl}-3,4,4-trimethyl-1,2-dioxetane **2** bzw. **3** sind geeignete Substrate für die Funktionalisierung mit protischen Nucleophilen. So wurden aus **2** z. B. mit Methanol, Laurylalkohol und Cholesterol die Dioxetane **4a–c** und mit Phenol und Thiophenol **4d** und **4e** dargestellt. Mit Acetonoxim und Benzaldoxim wurden unter basischen Bedingungen die Dioxetane **5a** und **5b** gebildet. Die Bis-dioxetane **6a** und **6b** konnten in guten Ausbeuten durch Reaktion von **2** mit Ethylendiamin und Hydrazin erhalten werden. Glycin und dessen Ethylester lieferten die Dioxetane **7a, b**, Ethyl-phenylalanat reagierte zu **7c**. Das Dipeptid-substituierte Dioxetan **7d** entstand aus L-Phenylalanyl-L-leucin, während Anilin und **3** zu 3,3,4-Trimethyl-4-{[(phenylsulfamoyl)carbamoyloxy]methyl}-1,2-dioxetan (**8**) führten. Durch Anwendung der aufgezeigten Synthesestrategie wurde eine Vielzahl von funktionalisierten Dioxetanen für photobiologische Tests als photogentoxische Substanzen zugänglich.

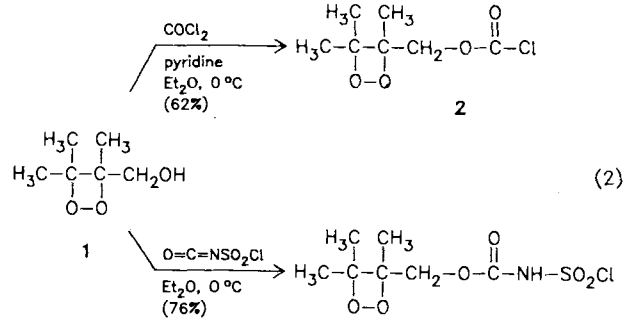
Although 1,2-dioxetanes are thermally labile substances, fragmenting on heating into electronically excited carbonyl products (Eq. 1), usually triplet states[1], recently derivatives have been prepared by functional group interconversion[2]. Therewith it was demonstrated that chemical transformations can be performed on these sensitive compounds, provided that appropriately mild conditions are employed. In view of their unique property of constituting latent excited states, specifically triplet states, biomolecules functionalized with dioxetanes (biodioxetanes) could serve as potential photogenotoxic agents. Indeed, it was recently[3] demonstrated that the functionalized dioxetanes **1** and **1a** exhibit genotoxicity in experiments with bacteria and cells, presumably of photochemical origin. Consequently, appropriate biodioxetanes should represent useful substances for photobiological studies and phototherapeutic exploration.





In our previous functionalizations[2a–c], the nucleophilic hydroxy handle in the dioxetane **1** was attached to electrophilic partners, including carboxylic acids and their halides, isocyanates, chloroformates, etc. However, most biomolecules abound with nucleophilic functional groups, e.g. hydroxy, sulfhydryl, amino, etc. These require dioxetanes with electrophilic handles for the expedient preparation of such biodioxetanes.

A convenient entry into dioxetanes with electrophilic functional handles is to employ the concept umpolung. The feasibility of this synthetic methodology was already demonstrated[2b] for the hydroxy-substituted dioxetane **1**, which was converted into its chlorocarbonyl derivative **2** by means of phosgene and into its *N*-(chlorosulfonyl)carbamate **3** by means of chlorosulfonyl isocyanate (Eq. 2).



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Considering that these chemical transformations entail the labile dioxetane **1**, the reported yields[2b] are exceptionally high. Thus, electrophilic dioxetanes **2** and **3** are now available for functionalization with nucleophilic partners. In this paper we report such transformations with alcohols, phenol, thiophenol, oximes, ethylenediamine, hydrazine, α-amino acids and esters, and a dipeptide.

Results and Discussion

The results for the electrophilic dioxetane **2**, prepared as previously described[2b], are collected in Scheme 1, clearly showing that a variety of nucleophiles can be linked to the dioxetane **2** in fair to excellent yields. In view of the labile nature of the dioxetanes **4**–**8**, mainly during isolation and purification (low-temperature silica gel chromatography), frequently appreciable quantities of the precious dioxetanes are lost by thermal decomposition. Although in the preparation of some of these dioxetanes alternative reaction conditions were employed, in Scheme 1 and the Experimental Section those conditions are reported which we consider more convenient and appropriate. The quality and purity of the dioxetanes rather than their yields dictated our choise of conditions. The dioxetanes **4**–**8** could be obtained as analytically pure substances, most of them in crystalline form.

Carbonate-Functionalized Dioxetanes 4a–e

Among the carbonates **4a**–**e**, clearly the present methodology of attaching the nucleophile (alcohol, phenol, or thiophenol) to the electrophilic chlorocarbonyl-substituted dioxetane **2** proved advantageous. Thus, the methoxycarbonyl-substituted dioxetane **4a** was obtained in 83% yield from **2** and methanol with pyridine as base, which is to be contrasted with a previous 39% yield linking the (hydroxymethyl)dioxetane **1** to the chloroformate derivative of methanol[2c].

For the long-chain lauryl alcohol an amine base proved ineffective, so that the alcoholate was used. Lithium laurate, prepared from the alcohol by treatment with *n*-BuLi, gave better yields of the lauryldioxetane **4b** than the potassium alcoholate, available from potassium hydride and the alcohol. In the case of the sterically encumbered cholesterol, the potassium alcoholate was used, affording the steroidal dioxetane **4c** in poor yields (14%). This latter case represents no improvement of our previous methodology[2c]. Triethylamine as base directly with the steroidal alcohol and **2** failed to give the desired dioxetane **4c**; cholesterol was recovered. Consequently, for reactive alcohols tertiary amines (pyridine or triethylamine) are advantageous, while for long-chain and sterically hindered alcohols the corresponding alcoholates work better in functionalizing dioxetane **2**.

Also phenol reacted well with **2** using triethylamine as base, affording the carbonate dioxetane **4d** in 79% yield. Thus, the more acidic phenol presents no problems in linking it to the electrophilic dioxetane **2** under base catalysis.

Although sulfur nucleophiles destroy dioxetanes[4] in complex reactions, it was of interest to functionalize thiophenol with the electrophilic dioxetane **2**. For successful preparation of the thiocarbonate dioxetane **4e**, it was critical to conduct the workup quickly and tying up excess thiophenol in form of its insoluble mercury salt by adding mercuric trifluoroacetate. Even small amounts of unreacted thiophenol left in contact with the dioxetane **4e** for longer periods led to substantial destruction of the latter. The use of lead thiophenolate in the presence of pyridine gave only a 16% yield of **4e** and thus represented no advantage over employing the free thiophenol directly. Once purified, the thiocarbonate dioxetane **4e** was perfectly stable, to be contrasted with other sulfur-substituted dioxetanes which possess short lifetimes[5]. Thus, the electron-withdrawal by the carbonate moiety reduces the nucleophilicity of the sulfur sufficiently, resulting in the thermally labile but isolable thiocarbonate-substituted dioxetane **4e**.

Oxime-Functionalized Dioxetanes 5a, b

These two derivatives of the (chlorocarbonyloxymethyl)dioxetane **2** were prepared by treating **2** with the anions of acetone oxime and of benzaldoxime, respectively, in 63% yield for **5a** and 31% for **5b**. In these cases aqueous NaOH in CH_2Cl_2 as biphasic system was found to be advantageous. This type of functionalization allows in principle binding electrophilic dioxetanes to biologically interesting aldehydic and ketonic substrates by means of their nucleophilic oxime derivatives.

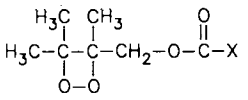
Carbamate-Functionalized Bis-dioxetanes 6a, b

Previously[2b] we showed that primary and secondary amines can be readily linked to the electrophilic dioxetane **2**, resulting in carbamate-functionalized dioxetanes. It was of interest to utilize diamines as nucleophiles, since this would make accessible bis-dioxetanes, a class of dioxetanes of which only few examples are known at this time[6]. Such bis-dioxetanes should be potentially effective photogenotoxic agents in view of their propensity for cross-linking of DNA[7]. Both ethylenediamine and hydrazine could be converted into the bis-dioxetanes **6a** and **6b**, respectively, in 61 and 68% yields. These bis-dioxetanes were quite labile, suffering decomposition at room temperature (ca. 20°C) within a few hours. These first representatives of such bis-dioxetanes, which are now readily available by this methodology, provide ample opportunity for photobiological investigation. Should the need arise, in principle the way is open to convert polyamines into the corresponding polydioxetanes via the carbamate linkage by employing the electrophilic dioxetane **2**.

Amino Acid-Functionalized Dioxetanes 7a–d

Since amino acids constitute essential biomolecules and under alkaline conditions exhibit substantial nucleophilic character, it was of interest to attempt functionalizing such nucleophiles with the electrophilic chloroformate dioxetane **2**. Indeed, glycine could be converted in 62% to the dioxetane **7a** via the carbamate linkage, using aqueous sodium hydroxide as base and H_2O/CH_2Cl_2 as biphasic medium. Critical for success was the workup procedure! Attempts to remove the water by rotoevaporation led to complete de-

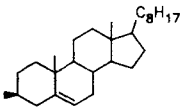
Scheme 1



4a–e

4a: X = OCH_3 (i-a) pyridine, MeOH, Et_2O, 0 °C (83%)

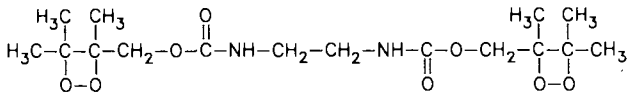
4b: X = O-*n*-$C_{12}H_{25}$ (i-b) *n*-$C_{12}H_{25}OH$, Et_2O, *n*-BuLi, 0 °C (40%)



4c: X = –O (i-c) KH, Et_2O, cholesterol, –60 °C/0 °C (14%)

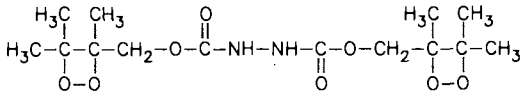
4d: X = OPh (i-d) NEt_3, Et_2O, PhOH, 0 °C (79%)

4e: X = SPh (i-e) 1) NEt_3, Et_2O, PhSH, 0 °C 2) $(CF_3CO_2)_2Hg$, 0 °C (53%)



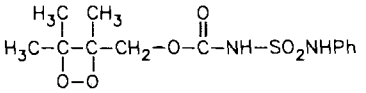
6a

6a: (iii-a) $H_2N-CH_2-CH_2-NH_2$, CH_2Cl_2, 0 °C (61%)

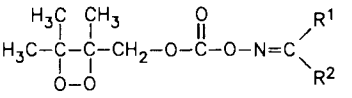


6b

6b: (iii-b) $H_2N-NH_2 \cdot HCl$, K_2CO_3, CH_2Cl_2, 0 °C (68%)



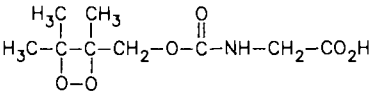
8 (11% from **3**)



5a, b

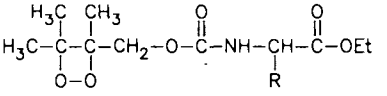
5a: $R^1 = R^2 = CH_3$ (ii-a) $HO-N=C(CH_3)_2$, NaOH, H_2O, Et_2O, 0 °C (63%)

5b: R^1 = H, R^2 = Ph (ii-b) $HO-N=C(H)Ph$, NaOH, H_2O, Et_2O, 0 °C (31%)



7a

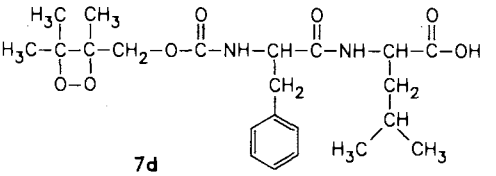
7a: (iv-a) $H_2N-CH_2-CO_2H$, NaOH, H_2O/CH_2Cl_2, 0 °C (62%)



7b, c

7b: R = H (iv-b) $HCl \cdot H_2N-CH_2-CO_2Et$, H_2O/CH_2Cl_2, NaOH, 0 °C (95%)

7c: R = $PhCH_2$ (iv-c) $HCl \cdot H_2N-CH(CH_2Ph)-CO_2Et$, Et_2O, NEt_3, 0 °C (92%)



7d

7d: (iv-d) L-phenylalanyl-L-leucine, H_2O/CH_2Cl_2, NaOH, 0 °C (47%)

struction of **7a**. To circumvent these problems, the entire aqueous phase containing **7a** was directly placed on the silica gel column at ca. 0 °C, conducting the subsequent elution with CH_2Cl_2/ether (1:2) at ca. –30 °C. This unconventional technique served its purpose well in view of the high yield (62%) of glycine dioxetane **7a** that could be achieved.

The functionalization of ethyl glycinate and phenylalanate with the electrophilic dioxetane **2** proceeded unproblematically. Using Et_3N or aqueous NaOH as base, the dioxetanes **7b** and **7c** could be obtained in 95 and 92% yields, respectively, after purification. These exceptionally high yields for dioxetane transformations encouraged us to link a dipeptide to **2** via the carbamate functionality. Indeed, L-phenylalanyl-L-leucine was converted into the dipeptide-substituted dioxetane **7d** in 47% yield using aqueous NaOH as base and a H_2O/CH_2Cl_2 biphasic medium. Clearly, the way is paved for the preparation of dioxetane-labeled polypeptides. Such unusual materials should stimulate novel photobiological experimentation.

Carbamate-*N*-sulfonamide-Functionalized Dioxetane 8

As an alternative electrophilic dioxetane for the functionalization with nucleophiles serves the derivative **3**, readily available in high yield (76%; Eq. 2) by reaction of the (hydroxymethyl)dioxetane **1** with chlorosulfonyl isocyanate. Treatment of dioxetane **3** with aniline (two equivalents) afforded the dioxetane **8** only in 11% yield. The difficulty was the isolation and purification of this rather polar dioxetane, which led to substantial decomposition. Although the electrophilic dioxetane **3** is readily available, we forsee at this

point no particular advantage over the chloroformate dioxetane **2**. For this reason we did not pursue any further functionalization of **3** with additional nucleophiles.

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Experimental

Boiling and melting points are uncorrected, the latter were taken on a Reichert Thermovar Kofler apparatus. – Infrared spectra: Beckman Acculab 4. – ^{1}H-NMR spectra: Hitachi-Perkin-Elmer R 24 B (60 MHz), Varian EM 390 (90 MHz), or Bruker WM 400 (400 MHz), TMS internal standard. ^{13}C-NMR spectra: Bruker WM 400 (100.6 MHz), $CDCl_3$ or TMS as internal standard. Mass spectra (MS): Varian MAT CH 7.

Combustion analyses for elemental composition: obtained in-house. – Thin-layer chromatography (TLC): Polygram SIL/G/UV (40 × 80 mm) from Machery and Nagel Co. – Column chromatography: silica gel 32–64 mesh ASTM (activity grade III).

Commercial reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Known compounds were prepared according to literature procedures. Unless otherwise stated, stirring was performed magnetically, room temperature was ca. 20°C, drying after aqueous workup was carried out with $MgSO_4$ and rotoevaporation was performed at aspirator pressure (15–20 Torr) at 0°C.

Caution: Dioxetanes are thermally labile peroxides and thus potentially dangerous materials (**Explosion**) so that all precautionary measures such as safety shield, face mask, and heavy gloves should be used when working with them. Only samples containing less than 1.0 g of crude material by theory should be utilized in the workup!

3-[(Methoxycarbonyloxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (**4a**): A 50-ml flask, provided with a 25-ml dropping funnel and an ice bath, was charged with a solution of 277 mg (3.50 mmol of pyridine in ca. 1 ml of anhydrous methanol. Under vigorous stirring and cooling at ca. 0°C was added a solution of 681 mg (3.50 mmol) of 3-[(chlorocarbonyloxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (**2**)[2b] in 15 ml of anhydrous ether. Within ca. 10 s a colorless precipitate (pyridine hydrochloride) separated. After ca. 5 min additional stirring was added 20 ml of 5% aqu. HCl, the organic phase separated, washed with saturated aqu. Na_2CO_3 (20 ml) and with water (20 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent afforded the crystalline crude **4a**, which was purified by flash chromatography on silica gel (16:1 adsorbant/substrate ratio, at −30°C, CH_2Cl_2 as eluant), followed by recrystallization from CH_2Cl_2/petroleum ether (30–50°C) (1:1); 553 mg (83%), yellow needles, m.p. 48–49°C (ref.[2c] 48–49°C).

3-[(Lauryloxycarbonyloxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (**4b**): A 100-ml, three-necked flask, provided with a 25-ml pressure-equalized dropping funnel, nitrogen inlet and outlet tubes, and an ice bath, was charged under dry nitrogen with a solution of 932 mg (5.01 mmol) of lauryl alcohol in 20 ml of anhydrous Et_2O. While vigorously stirring and cooling at ca. 0°C, was added within 5 min a solution of *n*-BuLi in *n*-hexane (4.35 mmol; 2.09 ml of 2.08 M solution). After 5 min stirring at 0°C was added at once a solution of 856 mg (4.40 mmol) of dioxetane **2** in 30 ml of anhydrous Et_2O, stirred for 10 min, and 101 mg (1.00 mmol) of Et_3N in 10 ml of anhydrous Et_2O added within 1 min. The reaction mixture was stirred for an additional 5 min and 10 ml of 2 N HCl was administered. The organic phase was separated, washed with water (10 ml), and dried with $MgSO_4$ and Na_2CO_3. Rotoevaporation of the solvent and double flash chromatography on silica gel (16:1 and 50:1 adsorbant/substrate ratio, respectively, at −30°C, CH_2Cl_2 as eluant) afforded a yellow oil which on crystallization from petroleum ether (30–50°C) gave 606 mg (40%) of pale yellow scales of **4b**, m.p. 25–28°C (dec.); peroxide content > 96% by iodometry; R_f = 0.79 [TLC on silica gel, eluting with Et_2O/petroleum ether (30–50°C) 1:1]. – IR (CCl_4): 3010 cm^{-1}, 2960, 2935, 2860, 1758, 1470, 1395, 1385, 1380, 1370, 1270, 1252, 1150, 985, 880. – ^{1}H-NMR ($CDCl_3$, 90 MHz): δ = 0.70–1.87 (m; 23H, $CH_3[CH_2]_{10}$), 1.45 (s; 3H, CH_3), 1.48 (s; 3H, CH_3), 1.65 (s; 3H, CH_3), 4.18 (t; 2H, OCH_2), AB system (δ_A = 4.49, δ_B = 4.75, J = 11.4 Hz; 2H, CH_2O). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.21 (q; CH_3), 17.97 (q; CH_3), 22.19 (t; CH_2), 22.73 (q; CH_3), 23.92 (q; CH_3), 25.59 (t; CH_2), 28.47 (t; CH_2), 29.22 (t; CH_2), 29.41 (t; CH_2), 29.51 (t; CH_2), 29.59 (t; CH_2), 29.65 (t; CH_2), 31.93 (t; CH_2), 68.69 (t; CH_2O), 68.96 (t; CH_2O), 88.62 (s; C–OO), 89.13 (s; C–OO), 154.92 (s; C=O). – MS (70 eV): *m/z* (%) = 220(0.7), 205(3), 177(0.3), 105(1), 58(32), 43(100).

$C_{19}H_{36}O_5$ (344.5) Calcd. C 66.24 H 10.53
Found C 66.68 H 10.82

3-[(5-Cholestene-3β-yloxycarbonyloxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (**4c**): A 100-ml, three-necked flask, provided with a 25-ml pressure-equalizing dropping funnel, nitrogen inlet and outlet tubes, and an ice bath, was charged with 113 mg (2.83 mmol) of potassium hydride and 5 ml of anhydrous ether under nitrogen. While stirring and cooling at ca. 0°C was added a solution of 1.10 g (2.85 mmol) of cholesterol in 10 ml of anhydrous Et_2O. After ca. 90 min stirring at ca. 0°C a white flaky precipitate had separated and after additional 3 h no gas evolution (hydrogen) could be detected. The pale orange-colored reaction mixture was cooled to ca. −60°C by means of a MeOH/dry ice bath and while stirring was added a solution of 818 mg (2.82 mmol) of dioxetane **2** in 2 ml of anhydrous Et_2O. The precipitate slowly dissolved resulting in a pale yellow solution, which was stirred for an additional 90 min at 0°C. Subsequently 10 ml of 2 N HCl was administered, the organic phase separated, washed with saturated aqu. $NaHCO_3$ (5 ml) and with water (5 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent gave 1.00 g (65%) of crystalline **4c**, which was purified by flash chromatography on silica gel [53:1 adsorbant/substrate ratio, at −30°C, Et_2O/petroleum ether (30–50°C) (1:2)] resulting in 214 mg (14%) of pale yellow plates of **4c**, m.p. 98–104°C (dec.) (ref.[2c] 97–104°C, dec.).

3,3,4-Trimethyl-4-[(phenoxycarbonyloxy)methyl]-1,2-dioxetane (**4d**): A 100-ml flask, provided with a 25-ml dropping funnel and an ice bath, was charged with 788 mg (4.05 mmol) of dioxetane **2** in 25 ml of anhydrous CH_2Cl_2 and while stirring and cooling at ca. 0°C was added within 10 min a solution of 409 mg (4.05 mmol) of Et_3N and 373 mg (3.97 mmol) of phenol in 20 ml of anhydrous CH_2Cl_2. After 10 min stirring at 0°C, 10 ml of 2 N HCl was added, the organic phase separated, washed with water (10 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent and flash chromatography of the residue on silica gel (49:1 adsorbant/substrate ratio, at −30°C, CH_2Cl_2 as eluant), followed by recrystallization from CH_2Cl_2/petroleum ether (30–50°C) (1:5) gave 790 mg (79%) of yellow needles of **4d**, m.p. 38–40°C; R_f = 0.56 (TLC on silica gel, eluting with CH_2Cl_2). – IR (CCl_4): 3015 cm^{-1}, 2970, 2940, 2860, 1775, 1600, 1500, 1460, 1390, 1380, 1372, 1270, 1250, 1215, 1153,

1067, 1025, 990, 960. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.43 (s; 3H, CH_3), 1.49 (s; 3H, CH_3), 1.64 (s; 3H, CH_3), AB system (δ_A = 4.73, δ_B = 4.66, J = 11.4 Hz; 2H, CH_2O), 7.05–7.60 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.61 (q; CH_3), 21.86 (q; CH_3), 23.67 (q; CH_3), 69.54 (t; CH_2O), 88.37 (s; C–OO), 88.86 (s; C–OO), 120.71(d), 126.04(d), 129.33(d), 150.56(s), 153.19 (s; C=O). – MS (70 eV): *m/z* (%) = 252 (0.03; M^+), 220 (0.07; M^+ – O_2), 194 (0.3; M^+ – acetone), 151(0.07), 94 (100; $C_6H_5OH^+$), 77 (36; $C_6H_5^+$), 58 (13; acetone$^+$), 57(21), 43 (80; $C_2H_3O^+$).

$C_{13}H_{16}O_5$ (252.3) Calcd. C 61.90 H 6.39
Found C 61.80 H 6.77

3,3,4-Trimethyl-4-{[(phenylthio)carbonyloxy]methyl}-1,2-dioxetane (**4e**): A 250-ml flask, provided with a 25-ml dropping funnel and an ice bath, was charged with 30 ml of anhydrous CH_2Cl_2 containing 992 mg (5.10 mmol) of dioxetane **2**. While vigorously stirring and cooling at ca. 0°C was added within 1 min a solution of 520 mg (4.73 mmol) of thiophenol and 485 mg (4.80 mmol) of Et_3N in 10 ml of anhydrous CH_2Cl_2. After stirring for 5 min at ca. 0°C, 20 ml of 2 N HCl was added, the organic layer separated and washed with water (2 × 20 ml). To the CH_2Cl_2 solution was added 426 mg (1.00 mmol) of mercuric trifluoroacetate, stirred 2 min, and washed with water (20 ml). Without drying, the organic phase was rotoevaporated and the residue submitted to flash chromatography on silica gel [35:1 adsorbant/substrate ratio, at –20°C, CH_2Cl_2/petroleum ether (30–50°C) 1:2], affording 678 mg (53%) of **4e** as yellow oil, which could not be induced to crystallize; R_f = 0.68 (TLC on silica gel, eluting with CH_2Cl_2). – IR (CCl_4): 3090 cm^{-1}, 3080, 3010, 2990, 2940, 1730, 1480, 1440, 1380, 1180, 1125, 1088, 1025, 913, 710, 691, 670. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.37 (s; 3H, CH_3), 1.39 (s; 3H, CH_3), 1.58 (s; 3H, CH_3), AB system (δ_A = 4.73, δ_B = 4.55, J = 11.4 Hz; 2H, CH_2O), 7.17–7.70 (m; 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 18.00 (q; CH_3), 22.19 (q; CH_3), 23.80 (q; CH_3), 68.60 (t; CH_2O), 88.51 (s; C–OO), 88.95 (s; C–OO), 127.13(s), 129.20(d), 129.78(d), 134.90(d), 169.43 (s; C=O). – MS (70 eV): *m/z* (%) = 210 (0.4, M^+ – acetone), 137(1), 110(16), 84(24), 58(23), 57(10), 43(100).

$C_{13}H_{16}O_4S$ (268.3) Calcd. C 58.19 H 6.01
Found C 58.28 H 6.41

3-[(Isopropylidenaminooxycarbonyloxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (**5a**): A 100-ml flask, provided with a 25-ml dropping funnel and an ice bath, was charged with a solution of 785 mg (4.04 mmol) of dioxetane **2** in 15 ml of Et_2O and while stirring and cooling at ca. 0°C was added within 10 min a solution of 295 mg (4.04 mmol) of acetone oxime and 161 mg (4.03 mmol) of NaOH in 5 ml of water. After stirring at 0°C for ca. 70 min, the organic layer was separated, the aqueous phase washed with Et_2O (2 × 10 ml), and the combined organic phases were washed with saturated brine (10 ml). On drying with $MgSO_4$ and rotoevaporation of the solvent, the resulting yellow oil was submitted to flash chromatography on silica gel (29:1 adsorbant/substrate ratio, at –30°C, CH_2Cl_2 as eluant) and subsequent recrystallization from Et_2O/petroleum ether (30–50°C) (1:2) gave 586 mg (63%) of yellow cubes of **5a**, m.p. 62–63°C; R_f = 0.47 (TLC on silica gel, eluting with CH_2Cl_2). – IR (CCl_4): 3005 cm^{-1}, 2990, 2940, 1795, 1655, 1440, 1380, 1275, 1225, 1175, 1152, 1065, 990, 912, 895, 652, 630. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.55 (s; 3H, CH_3), 1.57 (s; 3H, CH_3), 1.73 (s; 3H, CH_3), 2.09 (s; 3H, CH_3), 2.13 (s; 3H, CH_3), AB system (δ_A = 4.67, δ_B = 4.50, J = 11.1 Hz; 2H, CH_2O). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 16.94 (q; CH_3), 17.60 (q; CH_3), 21.79 (q; CH_3), 21.98 (q; CH_3), 23.79 (q; CH_3), 69.20 (t; CH_2O), 88.68 (s; C–OO), 89.10 (s; C–OO), 153.74 (s; C=O), 164.23 (s; C=N). – MS (70 eV): *m/z* (%) = 174 (0.08; M^+ – acetone), 131(16), 101(36), 58(18), 57(44), 56(80), 43(100).

$C_{10}H_{17}NO_5$ (231.3) Calcd. C 51.94 H 7.41 N 6.06
Found C 51.66 H 7.39 N 5.73

3-[(Benzylidenaminooxycarbonyloxy)methyl]-3,4,4-trimethyl-1,2-dioxetane (**5b**): A 100-ml flask, provided with a 25-ml dropping funnel and an ice bath, was charged with a solution of 510 mg (2.62 mmol) of dioxetane **2** in 10 ml of Et_2O. While stirring vigourously and cooling at ca. 0°C was added within 5 min a solution of 339 mg (2.80 mmol) of benzaldoxime and 105 mg (2.63 mmol) of NaOH in 10 ml of H_2O. After 20 min additional stirring was added 5 ml of 2 N HCl, the organic layer separated, washed with water (10 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent and flash chromatography of the residue on silica gel [49:1 adsorbant/substrate ratio, at –40°C, eluting with Et_2O/petroleum ether (30–50°C) 1:3] gave after recrystallization (twice) from Et_2O/petroleum ether (30–50°C) (2:1) 225 mg (31%) of yellow needles of **5b**, m.p. 96–97°C; R_f = 0.58 (TLC on silica gel, eluting with CH_2Cl_2). – IR (CCl_4): 3090 cm^{-1}, 3050, 3020, 3000, 2960, 1815, 1460, 1400, 1390, 1380, 1250, 1190, 1165, 1000, 975, 930, 870, 705. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.47 (s; 3H, CH_3), 1.50 (s; 3H, CH_3), 1.67 (s; 3H, CH_3), AB system (δ_A = 4.82, δ_B = 4.65, J = 11.1 Hz; 2H, CH_2O), 7.18–7.88 (m; 5H, C_6H_5), 8.35 (s; 1H, –CH=N–). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.73 (q; CH_3), 22.07 (q; CH_3), 23.87 (q; CH_3), 69.54 (t; CH_2O), 88.62 (s; C–OO), 89.16 (s; C–OO), 128.26(d), 128.81(d), 129.05(s), 131.90(d), 153.40 (s; C=O), 156.13 (d; –CH=N–). – MS (70 eV): *m/z* (%) = 221 (0.6; M^+ – acetone), 161 (0.4), 105(13), 104(21), 103(31), 77(16), 76(14), 58(17), 43(100).

$C_{14}H_{17}NO_5$ (279.3) Calcd. C 60.21 H 6.13 N 5.02
Found C 60.53 H 6.28 N 5.00

3,3'-[1,2-Ethandiylbis(carbamoyloxymethylene)]bis(3,4,4-trimethyl-1,2-dioxetane) (**6a**): A 100-ml flask, provided with 25-ml dropping funnel and an ice bath, was charged with a solution of 900 mg (4.63 mmol) of dioxetane **2** in 50 ml of dry CH_2Cl_2. While stirring and cooling at ca. 0°C was added within 10 min a solution of 278 mg (4.63 mmol) of ethylenediamine in 20 ml of dry CH_2Cl_2. After 5 min additional stirring of the opaque reaction mixture, 5 ml 2 N HCl was added, the organic phase separated, washed with water (10 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent afforded crystalline **6a**, which was submitted to flash chromatography on silica gel (50:1 adsorbant/substrate ratio, at –35°C, Et_2O as eluant). Recrystallization (twice) from CH_2Cl_2/petroleum ether (30–50°C) (1:1) gave 530 mg (61%) of yellow crystalline powder of **6a**, m.p. 104–105°C; peroxide titer >98% by iodometry; R_f = 0.35 (TLC on silica gel, eluting with Et_2O/CH_2Cl_2 1:1). – IR ($CHCl_3$): 3460 cm^{-1}, 3000, 2980, 2938, 2855, 1725, 1518, 1470, 1375, 1255, 1220, 1148, 1030. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 1.43 (s; 12H, CH_3), 1.61 (s; 6H, CH_3), 3.25–3.38 (m; 4H, CH_2N), 4.53 (s; 4H, CH_2O), 5.23 (br. s; 2H, NH). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.64 (q; CH_3), 21.98 (q; CH_3), 23.98 (q; CH_3), 40.95 (t; CH_2N), 66.48 (t; CH_2O), 89.19 (s; C–OO), 89.28 (s; C–OO), 156.42 (s; C=O). – MS (70 eV): *m/z* (%) = 242(1), 227(0.8), 224(0.9), 143(4), 125(6), 58(27), 43(100).

$C_{16}H_{28}N_2O_8$ (376.4) Calcd. C 51.06 H 7.50 N 7.44
Found C 51.39 H 7.70 N 7.26

3,3'-[1,2-Hydrazindiylbis(carbonyloxymethylene)]bis(3,4,4-trimethyl-1,2-dioxetane) (**6b**): A 100-ml flask, provided with a 25-ml dropping funnel and an ice bath, was charged with 360 mg (5.26 mmol) of hydrazine hydrochloride, 829 mg (6.00 mmol) of K_2CO_3, and 20 ml of CH_2Cl_2. While vigorously stirring this suspension at

ca. 0°C was added a solution of 1.04 g (5.35 mmol) of dioxetane **2** in 60 ml of CH_2Cl_2 followed by 5 ml of H_2O. The two-phase mixture was vigorously stirred at ca. 0°C for 2 h, the organic phase separated, washed with H_2O (20 ml), and dried with $MgSO_4$. Rotoevaporation of the solvent and flash chromatography on silica gel (53:1 adsorbant/substrate ratio, at −30°C, Et_2O as eluant) gave after recrystallization (twice) from CH_2Cl_2/petroleum ether (30−50°C) (2:1) 620 mg (68%) of yellow plates of **6b**, m.p. 93−95°C; peroxide titer >98% by iodometry; R_f = 0.59 (TLC on silica gel, eluting with Et_2O). − IR ($CHCl_3$): 3430 cm^{-1}, 3000, 2980, 1747, 1490, 1372, 1211, 1170, 1150, 1065, 985. − ^1H NMR ($CDCl_3$/[D_6]acetone 1:1, 90 MHz): δ = 1.52 (s; 12H, CH_3), 1.70 (s; 6H, CH_3), AB system (δ_A = 4.74, δ_B = 4.61, J = 11.7 Hz; 4H, CH_2O), 7.87−8.47 (br. s; 2H, NH). − ^{13}C NMR ($CDCl_3$/[D_6]acetone 1:1, 100.6 MHz): δ = 17.78 (q; CH_3), 22.17 (q; CH_3), 23.96 (q; CH_3), 67.06 (t; CH_2O), 89.12 (two s; C−OO), 156.73 (s; C=O). − MS (70 eV): *m/z* (%) = 206(0.3), 157(1), 149(1), 132(2), 58(34), 43(100).

$C_{14}H_{24}N_2O_8$ (348.4) Calcd. C 48.27 H 6.94 N 8.04
Found C 48.51 H 6.89 N 8.28

N-(3,4,4-Trimethyl-1,2-dioxetan-3-ylmethoxycarbonyl)glycine (**7a**): A 50-ml flask was charged with a solution of 296 mg (4.05 mmol) of glycine and 164 mg (4.09 mmol) of NaOH in 3 ml of H_2O. While stirring vigorously and cooling at ca. 0°C by means of an ice bath was added a solution of 803 mg (4.13 mmol) of dioxetane **2** in 40 ml of CH_2Cl_2, followed by a solution of 164 mg (4.09 mmol) of NaOH in 2 ml of H_2O. The CH_2Cl_2 was rotoevaporated and the yellow suspension was stirred vigorously at ca. 0°C for 7 h. After this time a clear yellow solution resulted, to which under vigorous stirring while cooling at ca. 0°C was added dropwise 2 N HCl (one drop every 10 s) until pH ≈ 2.5 was reached. The cold reaction mixture was as such transferred to a chromatography column containing 20 g of silica gel and CH_2Cl_2. While cooling at ca. 0°C, nitrogen pressure was applied until the liquid level was flush with the upper adsorbant level, then elution followed with CH_2Cl_2/Et_2O (1:2). When the yellow product front had advanced ca. 2 cm down from the upper adsorbant level, the temperature of the external cooling jacket was dropped to ca. −20 to −30°C. In this way clogging of the column due to crystallization of water could be avoided. Attempts to remove the water at reduced pressure prior to flash chromatography led to complete decomposition of the dioxetane **7a**. Recrystallization of the flash-chromatographed product from Et_2O/petroleum ether (30−50°C) (1:1) gave 582 mg (62%) of yellow needles of **7a**, m.p. 82−83°C (dec.); peroxide titer >98% by iodometry; R_f = 0.28 (TLC on silica gel, eluting with CH_2Cl_2/Et_2O 2:1). − IR ($CHCl_3$): 3600−2500 cm^{-1}, 3020, 2970, 2910, 1750, 1535, 1450, 1420, 1390, 1275, 1235, 1160, 1112, 1065. − ^1H NMR ($CDCl_3$, 90 MHz): δ = 1.42 (s; 6H, CH_3), 1.65 (s; 3H, CH_3), 3.90−4.10 (m; 2H, CH_2N), 4.60 (s; 2H, CH_2O), 6.0−6.2 (m; 1H, NH), 9.8−11.0 (br. s; 1H, CO_2H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.51 (q: CH_3), 21.87 (q; CH_3), 23.77 (q; CH_3), 42.21 (t; CH_2N), 67.17 (t; CH_2O), 89.12 (two s; C−OO), 156.40 (s; NHC=O), 173.73 (s; CO_2H). − MS (70 eV): *m/z* (%) = 202(0.06; $M^+ - O_2$), 149(0.4), 115(0.6), 102(0.6), 85(0.5), 58(28), 43(100).

$C_9H_{15}NO_6$ (233.2) Calcd. C 46.35 H 6.48 N 6.01
Found C 46.31 H 6.74 N 6.04

Ethyl N-(3,4,4-Trimethyl-1,2-dioxetan-3-ylmethoxycarbonyl)glycinate (**7b**): A 100-ml flask, provided with an ice bath, was charged with a solution of 595 mg (3.06 mmol) of dioxetane **2** in 20 ml of CH_2Cl_2 and a solution of 427 mg (3.06 mmol) of ethyl glycinate hydrochloride in 8 ml of H_2O. While vigorously stirring to this two-phase mixture at ca. 0°C was added within 10 min a solution of 245 mg (6.12 mmol) of NaOH in 8 ml of H_2O and allowed to stir at ca. 0°C for an additional 30 min. The aqueous layer was separated, extracted with CH_2Cl_2 (2 × 20 ml), and the combined organic phases were dried with $MgSO_4$. The solvent was rotoevaporated and the residual yellow oil flash-chromatographed on silica gel [43:1 adsorbant/substrate ratio, at −30°C, Et_2O/petroleum ether (30−50) 1:1 as eluant], affording 760 mg (95%) of **7b** as yellow oil, which could not be induced to crystallize; R_f = 0.31 [TLC on silica gel, eluting with Et_2O/petroleum ether (30−50) 1:1]. − IR (CCl_4): 3450 cm^{-1}, 2985, 2940, 2910, 2875, 1740, 1513, 1478, 1465, 1445, 1375, 1350, 1240, 1200, 1150, 1055, 1025. − ^1H NMR ($CDCl_3$, 90 MHz): δ = 1.28 (t; J = 6.0 Hz, 3H, CH_3), 1.46 (s; 6H, CH_3), 1.63 (s; 3H, CH_3), 3.96 (d; J = 4.5 Hz; 2H, CH_2N), 4.23 (q; J = 6.0 Hz; 2H, CH_2CH_3), AB system (δ_A = 4.65, δ_B = 4.51, J = 11.4 Hz; 2H, CH_2O), 5.45−5.82 (m; 1H, NH). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 13.88 (q; CH_3), 17.58 (q; CH_3), 21.92 (q; CH_3), 23.71 (q; CH_3), 42.45 (t; CH_2N), 61.23 (t; CH_2O), 66.50 (t; CH_2O), 88.92 (two s; C−OO), 155.86 (s; NHC=O), 169.84 (s; C=O). − MS (70 eV): *m/z* (%) = 205(0.4), 185(6), 112(10), 101(7), 58(23), 43(100).

$C_{11}H_{19}NO_6$ (261.3) Calcd. C 50.57 H 7.33 N 5.36
Found C 50.29 H 7.49 N 5.56

Ethyl N-(3,4,4-Trimethyl-1,2-dioxetan-3-ylmethoxycarbonyl)-L-phenylalanate (**7c**): A 250-ml flask, provided with a drying tube, 250-ml dropping funnel, and an ice bath, was charged with 1.31 g (5.70 mmol) of ethyl L-phenylalanate hydrochloride and 50 ml of dry Et_2O. While vigorously stirring, to this suspension at ca. 0°C was added within 1 min a solution of 1.16 g (11.5 mmol) of Et_3N in 10 ml of Et_2O. After stirring for 10 min was added a solution of 1.75 g (9.00 mmol) of dioxetane **2** in 90 ml of dry Et_2O within 10 min. The mixture was stirred at 0°C for an additional 5 min and 10 ml of 2 N HCl was added. The organic layer was separated, washed with saturated aqu. $NaHCO_3$ (2 × 20 ml), and dried with $MgSO_4$. After rotoevaporation of the solvent, the crude product was purified by flash chromatography on silica gel [27:1 adsorbant/substrate ratio at −30°C, eluting with petroleum ether (30−50°C)/Et_2O 1:1], resulting in 1.85 g (92%) of pure **7c** as yellow oil, which could not be induced to crystallize; R_f = 0.16 [TLC on silica gel, eluting with petroleum ether (30− 50°C)/Et_2O 2:1]; $[\alpha]_D^{20}$ = − 3.0 (c = 10.5, acetone). − IR (CCl_4): 3440 cm^{-1}, 3035, 2980, 2925, 1730, 1500, 1370, 1340, 1195, 1150, 1065. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.20−1.30 (m; 3H, CH_3CH_2), 1.38 (s; 3H, CH_3), 1.40 (s; 3H, CH_3), 1.63 (s; 3H, CH_3), 3.06−3.17 (m; 2H, $C_6H_5CH_2$), 4.14−4.20 (m; 2H, CH_2CH_3), 4.60 (s; 2H, CH_2O), 4.59−4.69 (m; 1H, CH−NH), 5.45−5.50 (m; 1H, NH), 7.12−7.39 (m; 5H, C_6H_5). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 13.93 (q; CH_3), 17.69 (q; CH_3)*, 22.03 (q; CH_3), 23.79 (q; CH_3), 37.96 (t; $CH_2C_6H_5$)*, 54.67 (d; NHCC=O), 61.43 (t; CH_3CH_2O), 66.33 (t; CH_2O)*, 88.91 (two s; C−OO), 126.93(d), 128.37(d), 129.13(d), 135.48(s), 154.99 (s; NHC=O), 171.30 (s; C=O); *double signals due to diastereomers. − MS (70 eV): *m/z* (%) = 275(0.03), 205(0.9), 176(9), 131(6), 128(6), 91(42), 58(26), 57(6), 43(100).

$C_{18}H_{25}NO_6$ (351.4) Calcd. C 61.53 H 7.17 N 3.99
Found C 61.02 H 7.08 N 3.58

N-(3,4,4-Trimethyl-1,2-dioxetan-3-ylmethoxycarbonyl)-L-phenylalanyl-L-leucine (**7d**): A 100-ml flask, provided with an ice bath, was charged with a solution of 288 mg (7.20 mmol) of NaOH in 13 ml of H_2O. While stirring was added 1.00 g (3.59 mmol) of L-phenylalanyl-L-leucine and allowed to stir until a clear solution resulted (ca. 15 min). The reaction mixture was cooled to 0°C and while stirring vigorously was added a solution of 758 mg (3.90 mmol) of dioxetane **2** in 20 ml of CH_2Cl_2. Subsequently the CH_2Cl_2 was rotoevaporated and the reaction mixture vigorously stirred at ca. 0°C

for 5.5 h. Under vigorous stirring was added dropwise (one drop per ca. 10 s) 2 N HCl until pH ≈ 2.5 was reached. At this point voluminous flakes separated out, which were dissolved by adding 5 ml of CH_2Cl_2 while stirring and cooling at ca. 0°C. The yellow organic phase was separated, the solvent rotoevaporated and the residue flash-chromatographed twice on silica gel (6:1 and 20:1 adsorbant/substrate ratio, at −30°C, eluting with CH_2Cl_2/Et_2O 2:1), affording 735 mg (47%) of yellow plates, m.p. 82−85°C (dec.). Recrystallization (twice) from CH_2Cl_2/petroleum ether (30−50°C) (2:1) gave pure dioxetane **7d**, m.p. 85−86°C (dec.); R_f = 0.40−0.65 (TLC on silica gel, eluting with CH_2Cl_2/Et_2O 1:1); $[\alpha]_D^{20}$ = − 9.3 (*c* = 2.5, acetone). − IR ($CHCl_3$): 3600−2500 cm^{-1}, 3430, 3010, 2970, 2940, 2875, 1755, 1722, 1680, 1505, 1470, 1455, 1440, 1375, 1220, 1150, 1060. − ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 0.86−0.94 [m; 6H, $(CH_3)_2CH$], 1.30−1.36 (m; 2H, CH_2CHCO_2H), 1.40 (s; 3H, CH_3), 1.46 (s; 3H, CH_3), 1.55−1.65 [m; 1H, $(CH_3)_2CH$)], 1.69 (s; 3H, CH_3), 3.00−3.10 (m; 2H, $C_6H_5CH_2$), 4.42−4.60 (m; 2H, NHCHCONH and $CHCO_2H$), 4.75 (s; 2H, CH_2O), 5.90−6.00 (br. m; 1H, NH), 6.80−7.00 (br. m; 1H, NH), 7.19−7.28 (m; 5H, C_6H_5). − ^{13}C NMR ([D$_6$]acetone, 100.6 MHz): δ = 17.95 (q; CH_3), 21.80 (q; CH_3), 22.27 (q; CH_3), 23.20 (q; CH_3), 23.93 (q; CH_3), 25.15 [d; $CH(CH_3)_2$], 38.62 (t; CH_2)*, 41.21 (t; CH_2), 51.18 (d; CH), 56.69 (d; CH)*, 66.60 (t; CH_2O)*, 89.15 (s; C−OO), 89.29 (s; C−OO), 127.01(d), 128.74(d), 130.03(d), 138.00(s), 156.29 (s; OCN), 172.79 (s; C=O); 174.29 (s; C=O); *double signals due to diastereomers. − MS (70 eV): *m/z* (%) = 360(7), 331(3), 304(2), 262(27), 202(39), 131(75), 104(29), 91 (100; $C_6H_5CH_2^+$), 58(1), 57(5), 43(25).

$C_{22}H_{32}N_2O_7$ (436.3) Calcd. C 60.57 H 7.34 N 6.42
Found C 60.88 H 7.13 N 6.53

3,3,4-Trimethyl-4-{[(phenylsulfamoyl)carbamoyloxy]methyl}-1,2-dioxetane (**8**): A 100-ml flask, provided with a 25-ml dropping funnel protected with a $CaCl_2$ drying tube and an ice bath, was charged with a solution of 3.93 g (14.4 mmol) of **3**[2c] in 30 ml of dry $CHCl_3$. While stirring vigorously at ca. 0°C was added a solution of 2.67 g (28.7 mmol) of aniline in 20 ml of dry $CHCl_3$. An immediate colorless precipitate (aniline hydrochloride) formed. After 30 min stirring at 0°C 2 N HCl was added dropwise until pH ≈ 2.5 was reached, at which point the precipitate dissolved and the reaction mixture acquired a red color. The organic layer was separated, washed with saturated brine (2 × 20 ml), and dried with $MgSO_4$. The dark residue was flash-chromatographed three times on silica gel [19:1, 26:1, and 31:1 adsorbant/substrate ratios, respectively, at −30°C, eluting with petroleum ether (30−50°C)/Et_2O (1:1, first time) and with CH_2Cl_2/Et_2O (30:1, second and third time)], resulting in 542 mg (11%) of yellow cubes of **8**, m.p. 106−108°C (dec.). On recrystallization from Et_2O/petroleum ether (30−50°C) (2:1) the pure dioxetane **8** was obtained as crystalline powder, m.p. 110−111°C (dec.); R_f = 0.26 [TLC on silica gel, eluting with Et_2O/petroleum ether (30−50°C) 1:1]. − IR ($CHCl_3$): 3390 cm^{-1}, 3240, 3000, 2980, 2940, 2875, 1750, 1600, 1495, 1475, 1433, 1405, 1385, 1355, 1295, 1260, 1210, 1170, 1155, 1105, 1090, 855. − ^{1}H NMR ([D$_6$]acetone, 90 MHz): δ = 1.28 (s; 3H, CH_3), 1.32 (s; 3H, CH_3), 1.50 (s; 3H, CH_3), AB signal (δ_A = 4.59, δ_B = 4.50, *J* = 11.3 Hz; 2H, CH_2O), 6.93−7.47 (m; 5H, C_6H_5), 8.90−9.17 (br. s; 1H, NHC_6H_5), 9.58−11.00 (br. s; 1H, O=CNHSO$_2$). − ^{13}C NMR ([D$_6$]acetone, 100.6 MHz): δ = 17.57 (q; CH_3), 21.97 (q; CH_3), 23.93 (q; CH_3), 67.78 (t; CH_2O), 89.20 (s; C−OO), 89.41 (s; C−OO), 121.52(d), 125.61(d), 129.84(d), 137.67(s), 151.59 (s; C=O). − MS (70 eV): *m/z* (%) = 272 (0.4; M^+ − acetone), 244(3), 198(5), 155(3), 93(13), 92(15), 58(24), 43(100).

$C_{13}H_{18}N_2O_6S$ (330.4) Calcd. C 47.26 H 5.49 N 8.48
Found C 47.41 H 5.17 N 8.28

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