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REACTIONS OF CYCLIC OXALYL COMPOUNDS[1] - 32. PHOTOCHEMICAL AND THERMAL 2+2-CYCLOADDITIONS OF DIPHENYLKETENE AND DIPHENYLKETEN-N-(4-METHYL-PHENYL)-IMINE TO FIVE-MEMBERED HETEROCYCLIC 2,3-DIONES

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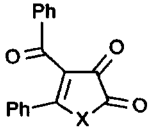
Abstract: *The heterocyclic 2,3-diones* 1 - 3 *have been found to undergo photochemical and thermal 2+2-cycloaddition reactions via their 3-carbonyl group to diphenylketene and the diphenylketen-N-(4-methylphenyl)-imine. These reactions afford rearranged cycloadducts as well as 2+2-cycloreversion products.*

Introduction

The oxa-1,3-diene system in 4-benzoyl substituted five-membered heterocyclic 2,3-diones 1 - 3, formed by the benzoyl group and the endocyclic C-C double bond, is capable to add isocyanides,[2,3] isocyanates,[4] carbodiimides[5] and ketenimines[6] leading to various bicyclic heterocycles.



1 X = O
2a X = N-Ph
2b X = N-Tol(p)
3 X = S

These reactions include 4+1 or 4+2-cycloaddition processes respectively and are usually accompanied by "long-range" Dimroth- or novel furandione-furandione rearrangements. Investigations of these rearrangements have successfully been made by use of ^{17}O-labeling.[7] Here we describe the thermal and photochemical behaviour of these diones 1 - 3 against diphenylketene and the related diphenylketen-N-(4-methylphenyl)-imine.

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Results and Discussion

Cycloaddition reactions of the furan-2,3-dione 1

When the 4-benzoyl-5-phenyl-furan-2,3-dione (1) is treated with diphenylketen-N-(4-methylphenyl)-imine for 4 hours at 60 °C in toluene, the yellow furo[3,2-c]pyridine derivative 4 can be obtained in 55% yield as the result of 4+2-cycloaddition processes and further rearrangements of the primary formed adduct[6]. In contrary, irradiation of 1 and the ketenimine in toluene, using a 150 W high pressure mercury lamp, for 2.5 hours at 17 °C affords the 3-diphenylmethylen-2(3H)-furanone 5 (scheme 1). In this case the reaction obviously is running via a 2+2 adduct 6 as intermediate and subsequent elimination of 4-methylphenyl-isocyanate.

Similar 2+2-cycloaddition- and 2+2-cycloreversion sequences in general are well known from the literature.[8] Constitution of 5 was elucidated with aid of an X-ray study (fig.1), which made evident an interesting stereochemical aspect: Two molecules of identical configuration, which can not be converted into each other by any symmetry-operation, form an asymmetric unit. The furan ring is planar.

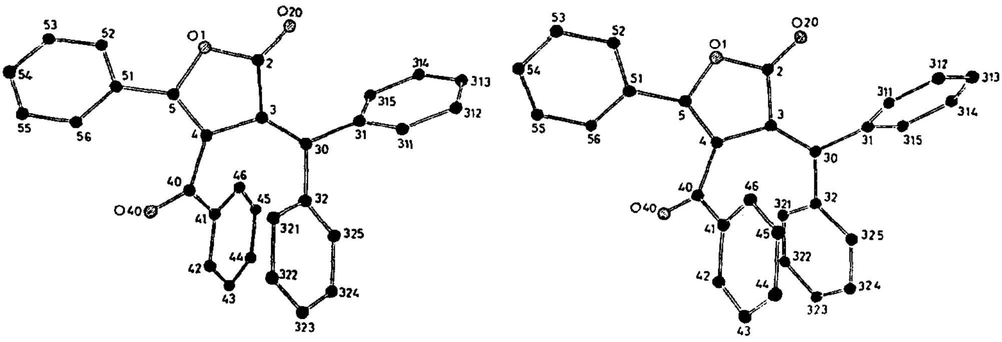
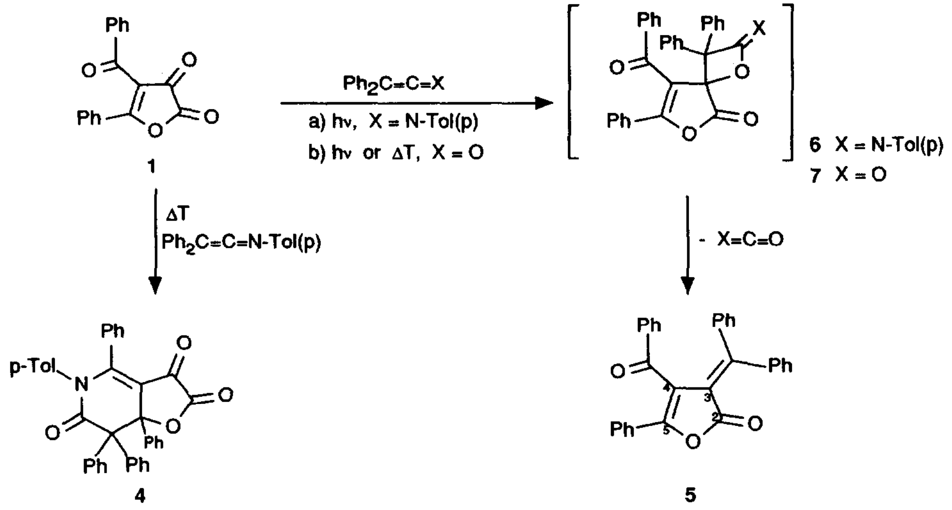


Fig.1. Perspective drawing of the molecule 5 without H-atoms. Black and hatched circles represent carbon and oxygen atoms, respectively.

With diphenylketene, the photoaddition to 1 in toluene (15 °C, 30 min) as well as the thermal reaction (60 °C, 2 hours) furnish the identical furan-2-one 5 in 45% and 72 %yield, respectively. With aid of UV spectroscopy (λ_{max}= 400 nm for 5, λ_{max}= 368 nm for 1) it was proofed by an independent experiment, that under conditions (15°C, toluene as solvent) the photo-reaction takes place, the observed concentration of the thermally formed reaction product is negligible.

The reaction pathways to 5 again involve a primary 2+2-cycloaddition step of the ketene to the C-3 carbonyl group in 1 leading to intermediate 7, which subsequently undergoes cycloreversion with elimination of CO_2 to form the corresponding 2(3H)-furanone 5. Analogous cycloaddition reactions of ketenes to carbonyl compounds are well known from the literature.[9,10]



Scheme 1.

Cycloaddition reactions of the pyrrol-2,3-diones 2a,b

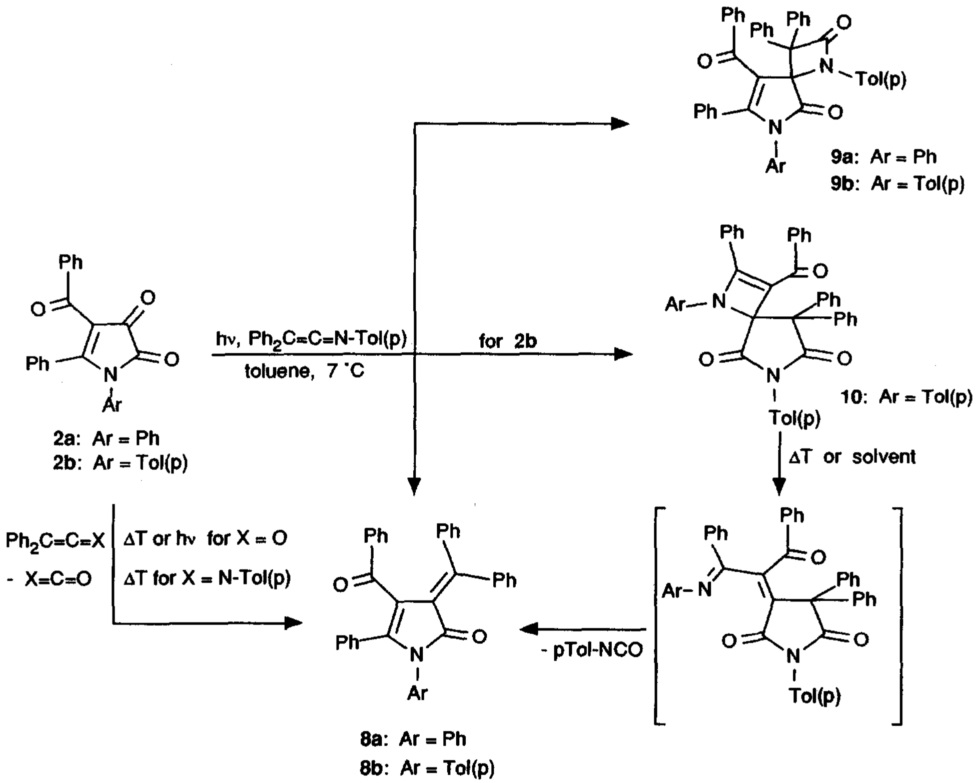
A more complex behaviour has been observed in the photo-reactions of the pyrrol-2,3-diones 2a,b with those heterocumulenes: 2a,b react with diphenylketene either thermally (110 °C, 2-3 min, without solvent) or photochemically (17 °C, 1.5 h, toluene) to give the 3-diphenylmethylen-2(3H)-pyrrolones 8a,b (scheme 2). Elucidation of the structure of 8a,b was made by comparison of their ^{13}C NMR and IR spectra with that of the furanone 5 and the educt 2a, (table 1). The spectrum of 8a exhibits the sp^2-ring carbons at δ = 165.6 (C-2), 116.8 (C-4), 156.0 (C-5). The signals at 192.2 and 148.0 are assigned to the sp^2-carbons of the benzoyl group and the exocyclic C-C double bond.

Table 1. ^{13}C NMR and IR data of compounds 1,5, 2a and 8a

Compound	^{13}C NMR shifts (ppm)^{a,b}					IR (cm^{-1})
	C-2	C-3	C-4	C-5	Ph-C=O	
1	153.3 (s)	175.7 (s)	116.6 (s)	177.1 (t)^{c}	188.6 (t)^{d}	1830 (s), 1720 (s), 1650 (m)
5	165.2 (s)	124.0 (s)	118.3 (s)	157.3 (t)^{e}	190.9 (t)^{f}	1770 (s), 1660 (s) 1580 (m), 1565 (m)
2a	157.0 (s)	178.4 (s)	112.6 (s)	173.2 (t)^{g}	187.8 (t)^{h}	1760 (s), 1640 (s), 1700 (m)
8a^{i}	165.6	j	116.8	156.0	192.2	1695 (s), 1640 (s), 1580 (m), 1565 (m)

a) Solvent CDCl$_3$. b) Shifts of aromatic C-atoms are not reported. c) J = 4.8 Hz. d) J = 4.0 Hz. e) J = 4.2 Hz. f) J = 4.0 Hz. g) J = 4.5 Hz. h) J = 4.0 Hz. i) Broadband decoupled spectrum. j) No distinct assignment possible due to overlap with signals of the aromatic C-atoms.

Thermic treatment of the pyrrol-2,3-dione 2a with an excess of diphenylketen-N-(4-methylphenyl)-imine at 100 °C for 70 hours gives an orange compound in moderate yield (36%). This compound was found to be identical with 8a by mp, TLC and IR spectrum (scheme 2).



Scheme 2.

Irradiation of the pyrrol-2,3-diones 2a,b and the diphenylketenimine (5 - 7 °C, 2.5 hours, toluene) leads to the formation of two (in case of 2a) or three (in case of 2b) isolable products, respectively. Their separation is accomplished by fractional crystallization from ethereal solution (see Experimental Part): The orange compounds in both cases crystallizing first came out to be the 3-diphenylmethylen-2(3H)-pyrrolones 8a,b.

The constitution of the 1:1 adducts 9a,b could be determined completely with aid of an X-ray analysis of 9a, which assigned them a diaza-spiro[3,4]octen-dione structure.

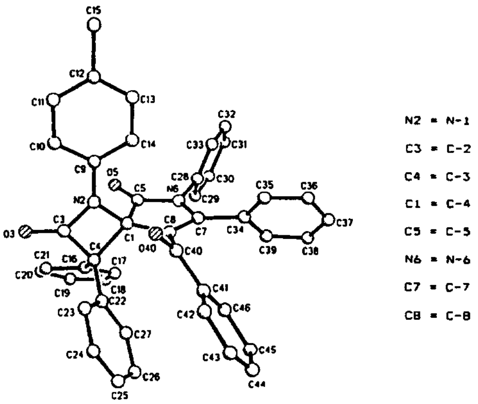
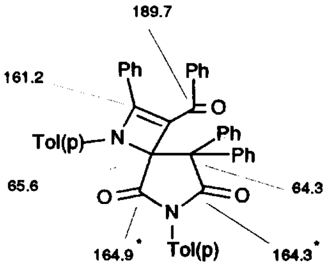


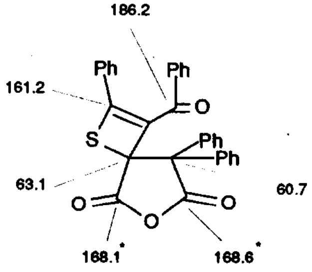
Fig.2. Perspective drawing of the molecule **9a** without H-atoms. White, dotted and hatched circles represent carbon, nitrogen and oxygen atoms, respectively.

In case of the pyrrol-2,3-dione **2b** in addition to **8b** and **9b** a further 1:1 adduct **10** is obtained: The IR-spectroscopic data of **10** [1800 cm^{-1}(m) and 1720 cm^{-1}(s)] indicate the presence of a succinimide moiety.[11] The proposed diaza-spiro[3,4]octen-dione structure for **10** was confirmed finally by comparison of the ^{13}C NMR data with those of the analogous spiro derivative **11**, the structure of which has been successfully clarified with aid of an X-ray study (see below).



10

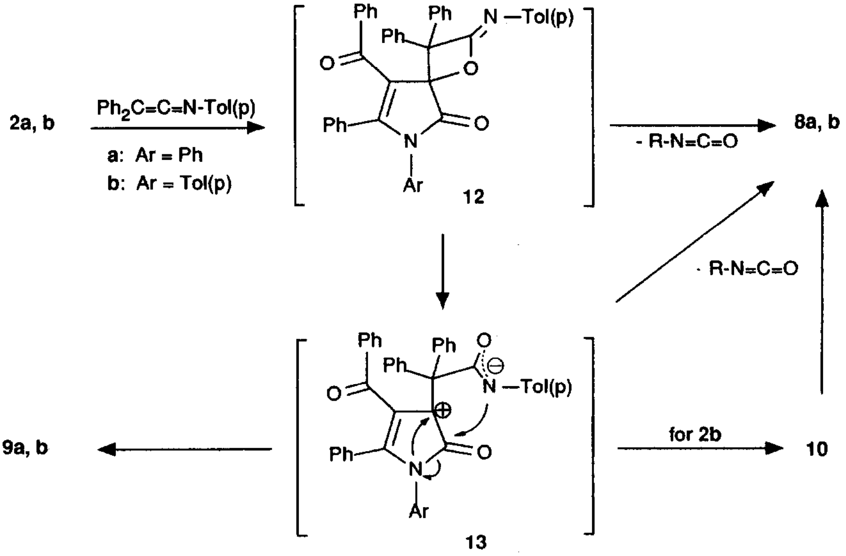
* exchangeable



11

Compound **10** is thermally labile and slowly rearranges into the pyrrolone **8b** and 4-methylphenylisocyanate in toluene or acetone solutions at room temperature. In the solid state the same reaction takes place only above 170 °C (no melting point can be obtained). The instability of this compound is probably caused by a valence isomerization of the spiro-connected azetine-ring to the corresponding open chain 1-aza-butadiene system.[12] This system contains a C=N-function which might initiate via nucleophilic attack the subsequent surprising electronic rearrangement with elimination of the isocyanate to form **8b**. Compound **8b** obviously is the most stable compound under those conditions. A similar reaction was also observed with the analogous spiro-thiete system **11** (see scheme 4).

The formation of **8a, b, 9a, b** and **10** should be started by a Paterno-Büchi reaction[13] involving the heterocumulene and the 3-carbonyl group of the pyrrol-2,3-dione **2**: The primary formed α-imino-oxetane derivative **12** is not isolable and either reacts with loss of isocyanate to the pyrrolones **8** or rearranges to the spiro compounds **9** and **10**. Similar 2+2-cycloadditions of ketenimines to the carbonyl group in quinones affording imino-oxetane derivatives, which rearrange into β-lactams, have been found by Ogino et al.[14]



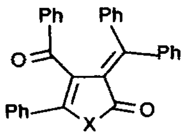
Scheme 3.

The rearrangements **12** → **9** and **12** → **10**, respectively are formulated via zwitterion **13** as intermediate. The formation of similar zwitterionic species are discussed for rearrangements of α-imino-oxetanes to β-lactames[9] since analogous dipoles with sufficient resonance stabilization even can be isolated.[8] The nucleophilic attack of the carboxylimidate nitrogen atom at the positively charged C-3-atom in the dipole **13** easily leads to the spiro-ß-lactam **9** (Dimroth rearrangement[15]). The formation of **10** should involve a nucleophilic attack of the carboxyl-imidate at the lactam carbonyl group forming the succinimide moiety and initiating a ring-contraction by synchronous or subsequent attack of the lactam nitrogen at the carbo-cation forming the azet ring (indicated by arrows with intermediate **13**).

Cycloaddition reactions of the thiophen-2,3-dione 3

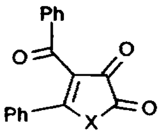
Heating at 90 °C or irradiation (toluene) of the thiophen-2,3-dione **3** in the presence of an excess of diphenylketene yields a mixture of the spiro-thiete **11** and the thiophen-2-one **14**. These compounds can be separated either by trituration of the mixture in ether/DME (1:1), thus dissolving **11** and keeping **14** as residue, or fractionated crystallization from benzene/glacial acetic acid (7:3). Finally, analytically pure samples of **11** and **14** are obtained by recrystallization from glacial acetic acid.

The structure of **14** (orange crystals) is assigned on the basis of IR, MS and NMR data. Of particular note are the similarities of the ^{13}C NMR and IR data of **14** with those of **5** in comparison with the parental compounds **1** and **3** (table 2).



5 X = O

14 X = S



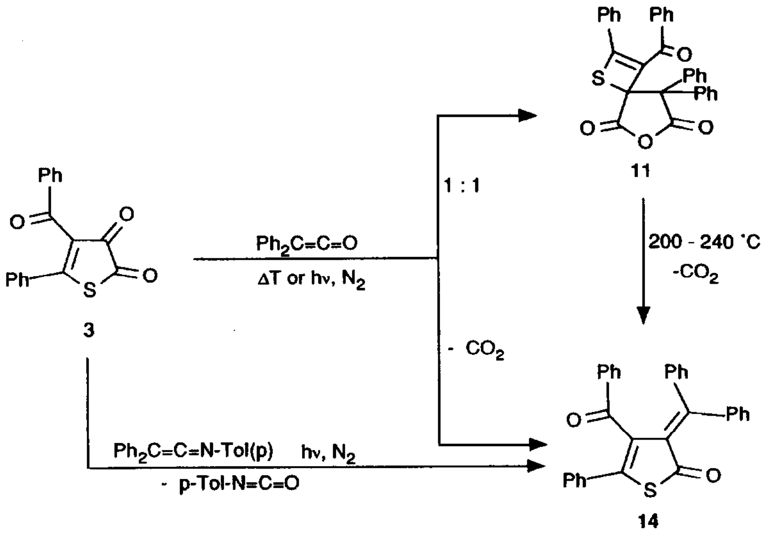
1 X = O

3 X = S

Table 2. ^{13}C NMR and IR data of compounds 3 and 14 (for compounds 1 and 5 see table 1)

Compound	^{13}C NMR shifts (ppm)[a,b]					IR (cm^{-1})
	C-2	C-3	C-4	C-5	Ph-$\underline{C}$=O	
3	181.3 (s)	183.4 (s)	c	168.9 (t)[d]	191.8 (t)[e]	1725 (m), 1695 (s), 1645 (s)
14	191.0 (s)	c	c	160.2 (t)[f]	192.1 (t)[g]	1685 (s), 1665 (s)

a) Solvent CDCl$_3$. b) Shifts of aromatic C-atoms are not reported. c) These values are within the region of the aromatic C-atoms and could therefore not be assigned precisely. d) J = 5.0 Hz. e) J = 4.6 Hz. f) J = 4.2 Hz. g) J = 4.0 Hz.



Scheme 4.

Compound **11** was found by elemental analysis and mass spectroscopy (m/e = 488) to be an 1:1 adduct of **3** and diphenylketene. Since the structure of **11** could not be clearly elucidated from its spectral parameters, an X-ray study of a single crystal of **11** was performed making evident an unusual 6-oxa-1-thia-spiro[3.4]octen skeleton (fig.3).

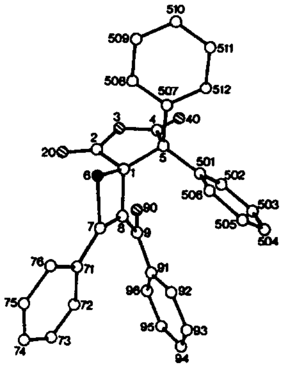
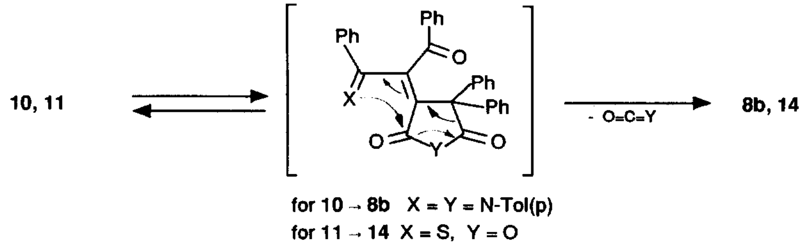


Fig.3. Perspective drawing of the molecule **11** without H-atoms. White, black and hatched circles represent carbon, sulphur, and oxygen atoms, respectively.

The thiete ring is nearly planar, the spiro angle is found to be 90.8°. Compared with the corresponding data for bond distances and bond angles of a similar spiro-thiete compound, derived from a 2+2-cycloaddition reaction of a thio-parabanic acid to diphenylacetylene,[16] the spiro-C-S bond is slightly shortened (6.2 pm), while the C-S-C angle is widened (1.8°). This could be due to the exchange of an electron donating substituent (N-Me) by an electron withdrawing one (C=O) of the spiro-C in **11**.

The reaction pathways to **11** and **14** should be analogous to those of **2b** and ketenimine to **8b** and **10** (scheme 3) and may involve also similar intermediates. Ring contraction reactions of S-heterocycles initiated by an nucleophilic attack of the sulphur are already known,[17] formation of an anhydride from a thioester reacting with a carboxylate ion has been observed too.[18] In analogy with **10** the thermolysis of **11** above 200 °C leads to the corresponding (3H)-thiophenone **14** but in contrary to **10**, **11** remains stable in solution even by heating at higher temperatures (100 - 120 °C). Electrocyclic ring opening leading to an open chain intermediate again could be an essential process.



Scheme 5.

Irradiation of the thiophene-2,3-dione **3** and the ketenimine (19 °C, 4 hours, toluene) produces **14** in low yield (10%), while the thermal reaction leads to a 4+2-cyloadduct as the main product[6] besides a small amount of **14** (< 5%).

Conclusion

Both - thermally and photochemically - initiated cycloaddition reactions of the 2,3-diones **1**, **2** and **3** with the diphenylketene and diphenylketen-N-(4-methylphenyl)-imine lead to formation of usual (**5**, **8**, **14**) and unusual (**9**, **10**, **11**) reaction products. Structure elucidation only was successful done with aid of several X-ray studies (compounds **5**, **9** and **11**) and extensive ^{13}C NMR spectroscopic measurements. The reaction pathways deduced from structural comparison of educts and the corresponding products offer conventional 2+2-cycloaddition and cycloreversion processes, respectively, besides surprising and unexpected rearrangements (**2** $\rightarrow$ **10**, **3** $\rightarrow$ **11**).

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra (IR) were recorded in KBr using a Perkin Elmer 298 spectrometer. Nuclear magnetic resonance spectra (^{13}C NMR) were determined on a Varian XL 200 spectrometer with tetramethylsilane as internal standard. Elemental analysis were performed with a Carlo Erba Elemental Analyser 1106. Electron impact mass spectra were recorded on a Hewlett-Packard 5930 (70 eV) and a Varian-MAT 111 (80 eV) instrument. Photolyses were performed in a Pyrex apparatus using a 150 W Hanau TQ 150 high-pressure mercury lamp. All reactions were carried out under a permanent nitrogen atmosphere. Solvents were dried according to standard procedures.

X-ray diffraction studies were carried out on a Syntex-P3 four-circle diffractometer with graphite monochromatized MoKα-radiation. Crystal structure determination was performed with SHELXTL[19] on an Eclipse S/250 computer. Special X-ray operations and results are listed in Table 3. The orientation matrix and the cell parameters were determined from transparent crystals of given dimensions. Measurement of intensities : ω-scan, 1° range, MoKα, $2\theta_{max} = 55°$. Solving by direct methods, refining by block-diagonal-matrix least-squares. The positions of hydrogen atoms are calculated geometrically and considered isotropically in all refinements.

*Thermal reaction of the furan-2,3-dione **1** with diphenylketene.* **1** (0.28 g, 1.0 mmol) reacted with diphenylketene (0.58 g, 3.0 mmol) at 60 °C for 2 h. The so formed orange residue was crystallized in dry ether and recrystallized from absolute ethanol to give 0.31 g (72%) of **5** as yellow rhombs; mp 185 - 186 °C; ^{13}C-NMR and IR data see table 1; MS (80 eV): m/z 428 (M^+,28), 323 (20), 295 (5), 189 (11). Anal. Calcd. for $C_{23}H_{20}O_3$: C, 84.08; H, 4.71. Found: C, 83.99; H, 4.83%.

*Photochemical reaction of the furan-2,3-dione **1** and N-(4-methylphenyl)-diphenylketenimine.* A solution of **1** (1.00 g, 3.6 mmol) and diphenylketen-N-(4-methylphenyl)-imine (1.02 g, 3.6 mmol) in toluene (370 ml) was irradiated at 15°C for 2.5 h. After evaporation of the solvent the residue was treated with ether to give 0.92 g (60 %) of **5**.

*Photochemical reaction of the furan-2,3-dione **1** and diphenylketene.* A solution of **1** (1.00 g, 3.6 mmol) and diphenylketene (0.75 g, 3.9 mmol) in toluene (370 ml) was irradiated for 6 h at 15 °C. After removal of the solvent and treatment of the residue with dry ether 0.70g (45%) **5** were obtained.

*Thermal reaction of the pyrrol-2,3-dione **2a** and diphenylketene.* In a reaction tube the pyrrol-2,3-dione **2a** (0.35 g, 1.0 mmol) and diphenylketene (0.58 g, 3.0 mmol) were mixed under nitrogen. The tube is dived into an oilbath preheated at 110 - 115 °C for 2-3 min. After cooling to 20°C the residue was crystallized in ether and purified from glacial acetic acid to give 0.44 g (87%) of **8a** as orange crystals; mp 255 °C. IR and ^{13}C NMR data see table 1; MS (80 eV): m/z 503 (M^+, 33), 475 (10), 426

(12), 398 (12), 180 (69), 105 (55), 77 (100). Anal. Calcd. for $C_{36}H_{25}NO_2$: C, 85.85; H, 5.01; N, 2.78. Found: C, 86.03; H, 5.31; N, 2.71%.

Photochemical reaction of **2a** *and diphenylketene*. A solution of the pyrrol-2,3-dione **2a** (0.75 g, 2.1 mmol) and diphenylketene (0.40 g, 2.1 mmol) in dry toluene (100 ml) was irradiated at 17 °C for 1.5 h. After evaporation of the solvent and addition of ether 0.49 g (68%) of **8a** were isolated, identical with the compound described above (IR, mp).

Thermal reaction of the pyrrol-2,3-dione **2b** *and diphenylketene*. Analogous to preparation of **2a** compound **8b** was obtained in 79% yield. mp 258 - 260 °C; IR(KBr): 1695, 1660 cm^{-1}. Anal. Calcd. for $C_{37}H_{27}NO_2$: C, 85.84; H, 5.27; N, 2.71. Found: C, 85.56; H, 5.38; N, 2.64%.

Photochemical reaction of **2b** *and diphenylketene*. A solution of the pyrrol-2,3-dione **2b** (0.50 g, 1.4 mmol) and diphenylketene (0.27 g, 1.4 mmol) in dry toluene (100 ml) was irradiated at 17°C for 1.5 h to give, after removal of the solvent, 0.30 g (43%) of **8b** as orange crystals.

Thermal reaction of the pyrrol-2,3-dione **2a** *with diphenyl-N-(4-methylphenyl)-ketenimine*. **2a** (0.35 g, 1.0 mmol) and the ketenimine (1.13 g, 4.0 mmol) were heated at 100 °C for 72 h. The crude residue is triturated in dry ether and recrystallized from glacial acetic acid to give 0.18 g (36 %) of **8a**.

Photochemical reaction of the pyrrol-2,3-diones **2a,b** *with diphenylketen-N-(4-methylphenyl)-imine*. A solution of the corresponding pyrrol-2,3-dione **2** (1.4 mmol) and the ketenimine (1.5 mmol) in dry toluene (100 ml) was irradiated for 2.5 h at 5 - 7 °C. After evaporation of the solvent in vacuo (bath temperature 30 °C) the oily residue was dissolved in dry ether:

a) From the reaction of **2a** fractions of enriched **8a** and **9a**, resp., were precipitating successively from the etheral solution, filtered and purified by recrystallization from glacial acetic acid. **8a**: yield 0.35 g (49%) orange crystals. mp 255 °C, identified by IR and mp. **9a**: 0.15 g (17%), light beige solid, melting at 230°C (decomposition interval 180 - 230°C); IR(KBr): 1755, 1745, 1640 cm^{-1}. Anal. Calcd. for $C_{44}H_{32}N_2O_3$: C, 83.00; H, 5.07; N, 4.40. Found: C, 82.69; H, 5.35; N, 4.16%.

b) In case of the reaction of **2b** after isolation and separation of **8b** and **9b**, performed as described above with **8a** and **9a**, an additional third fraction consisting of a mixture of **8b** and **10** was obtained from the etheral mother liquor. The separation of **8b** and **10** was carried out by stirring the mixture in ether (5 ml), where **10** dissolved and **8b** remained as a solid. After crystallization from the etheral solution **10** is purified by suspending in dry acetone with short slightly warming up to 30°C thus removing small amounts of impurities. **8b** and **9b** are purified as described above for **8a** and **9a**, resp. **8b**: 0.15 g (21%), orange crystals (from AcOH), identified by IR and mp. **9b**: 0.13 g (15%). mp. 230 °C (from AcOH). IR(KBr): 1755, 1745, 1640 cm^{-1}; ^{13}C-NMR (DMSO-d$_6$): δ = 186.8, 172.0, 162.8, 154.2, 140 - 120 (aromatic C-atoms), 109.3, 73.2, 72.0, 18.4, 18.2. Anal. Calcd. for $C_{45}H_{34}N_2O_3$: C, 83.05; H, 5.27; N, 4.30. Found: C, 82.77; H, 5.31; N, 4.39%. **10**: 0.2 g (23%). IR(KBr): 1800, 1720, 1665 cm^{-1}; ^{13}C NMR (acetone-D$_6$): δ = 189.7, 164.9, 164.3, 161.2, 140 - 120 (aromatic C-atoms), 65.6, 64.3, 20.9, 20.8. Anal. Calcd. for $C_{45}H_{34}N_2O_3$: C, 83.05; H, 5.27; N, 4.30. Found: C, 83.18; H, 5.33; N, 4.16%.

Thermolysis of **10**. 5 min heating of **10** (0.15 g, 0.23 mmol) at 230-235 °C led to a crude product, which was treated with ether and recrystallized from glacial acetic acid to give 0.075 g **8b** (64%), identified by IR, TLC and mp.

Thermal reaction of thiophen-2,3-dione **3** *and diphenylketene*. The thiophene-dione **3** (0.29 g, 1.0 mmol) and diphenylketene (0.49 g, 2.5 mmol) were heated at 90 °C for 5 min. The crude residue was triturated in dry ether and the two compounds **11** and **14**, resp. were separated by several fractional recrystallizations from benzene/glacial acetic acid (7:3). **11**: 0.05 g (10%) light yellow solid, which converts into **14** above 200 °C. IR(KBr): 1850, 1780 cm^{-1}; MS (70 eV): m/z 488 (M$^+$, 5), 460 (4), 444 (49), 416 (52), 339 (28), 165 (42), 121 (65), 105 (100), 77 (90). ^{13}C NMR (CDCl$_3$): δ = 186.2, 168.6, 168.1, 161.4, 140 - 120 (aromatic C-atoms), 63.1, 60.7. Anal. Calcd. for $C_{31}H_{20}O_4S$: C, 76.20; H, 4.13; S, 6.56. Found: C, 76.45; H, 4.37; S, 6.13%. **14**: 0.07 g (16%) orange needles, mp 249 - 251 °C (from AcOH). MS (80 eV): m/z 444 (M$^+$); ^{13}C-NMR and IR data see table 2. Anal. Calcd. for $C_{30}H_{20}O_2S$: C, 81.05; H, 4.54; S 7.21. Found: C, 81.14; H, 4.63; S, 7.02%.

Thermolysis of **11**. Rapid heating of **11** (0.05 g, 0.1 mmol) to 230 - 250 °C led with evolution of CO_2 to a dark red material, which crystallized by treating with anhydrous ether yielding 0.02 g (40%) of **14** (identified by mp and IR).

Photochemical reaction of thiophen-2,3-dione 3 and diphenylketene. A solution of the thiophene-2,3-dione **3** (1.00g, 3.4 mmol) and diphenylketene (0.75 g, 3.9 mmol) in absolute toluene (370 ml) was irradiated for 4.5 h at 15 °C. After evaporation of the solvent at 30 °C the residue was treated with ether and filtered. The crude material containing two main compounds (proven by TLC) was separated by stirring in a 1:1 mixture of ether/dimethoxyethane, where **11** dissolved and **14** remained as solid. Both compounds are purified finally by recrystallization from glacial acetic acid. **11**: 0.33 g (20%). **14**: 0.38 g (25%).

Photochemical reaction of thiophen-2,3-dione 3 and diphenylketen-N-(4-methylphenyl)-imine. A solution of **3** (1.00 g, 3.4mmol) and the ketenimine (1.00 g, 3.5 mmol) in dry toluene (370 ml) was irradiated for 4 h at 15 °C. Evaporation of the solvent and treatment of the residue with ether gave 0.15g (10%) of **14** which was recrystallized from glacial acetic acid.

Table 3. Crystal parameters for the X-ray diffraction study[20] of compounds **5**, **9a** and **11**

Compound	5	9a	11
formula	$C_{30}H_{20}O_3$	$C_{44}H_{32}N_2O_3$	$C_{31}H_{20}O_4S$
mol weight	428.5	636.8	488.6
crystal dimensions [mm]	0.25x0.5x0.15	0.75x0.85x0.7	0.35x0.55x0.1
crystal system	tricl.	monocl.	monocl.
space group	P$\bar{1}$ (no. 2)		P2_1/n (no.14)
lattice axes [Å]			
a	12.625 (6)	18.26 (1)	24.040 (3)
b	18.84 (1)	15.65 (1)	10.269 (2)
c	10.371 (7)	12.19 (1)	9.737 (2)
lattice angles [deg]			
α	91.63 (5)		
β	93.07 (4)	92.51 (7)	90.77 (2)
γ	107.26 (4)		
unit cell vol [Å^3]	2350.1 (8)	3482.0 (5)	2403.5 (4)
Z	4	4	4
$D_{calc.}$ [g.cm^{-3}]	1.211	1.214	1.350
reflections collected	3366	6602	3494
reflections observed [F ≥ 3σ(F)]	3346	4561	2938
residue factor (after anisotropic thermal parameter refinement)	0.033	0.065	0.046

Table 4. Atomic co-ordinates (x10^4) and eqivalent isotropic displacement parameters (Å^{2}x10^3) of compound **5**. Equivalent isotropic U is defined as $\frac{1}{3}$ of the trace of the orthogonalised U_{ij} tensor.

	molecule 1				molecule 2			
Atom	x	y	z	U_{eq}	x	y	z	U_{eq}
O(1)	2713(2)	4939(1)	-799(2)	57(1)	1917(2)	79(1)	-1018(2)	57(1)
C(2)	1773(2)	4485(2)	-219(3)	54(1)	2436(2)	-379(2)	-353(3)	54(1)
C(3)	2018(2)	4639(2)	1205(2)	50(1)	2392(2)	-201(2)	1052(2)	47(1)
C(4)	3098(2)	5233(2)	1348(2)	51(1)	1890(2)	415(2)	1094(2)	50(1)
C(5)	3494(2)	5388(2)	154(3)	51(1)	1647(2)	567(2)	-144(3)	51(1)
O(20)	1011(2)	4066(1)	-874(2)	72(1)	2764(2)	-826(1)	-928(2)	71(1)
C(30)	1405(3)	4223(2)	2121(3)	51(1)	2713(2)	-589(2)	2012(2)	49(1)
C(31)	254(2)	3681(2)	1855(2)	52(1)	3468(2)	-1056(2)	1761(2)	48(1)
C(32)	1888(2)	4279(2)	3481(3)	54(1)	2328(2)	-572(2)	3341(3)	52(1)
C(40)	3593(2)	5700(2)	2557(3)	57(1)	1893(3)	903(2)	2258(3)	58(1)
O(40)	4604(2)	5852(1)	2900(2)	82(1)	1045(2)	1075(1)	2515(2)	85(1)
C(41)	2813(3)	6017(2)	3285(3)	53(1)	2984(3)	1189(2)	3080(3)	56(1)
C(42)	3156(3)	6280(2)	4562(3)	68(1)	2930(3)	1424(2)	4358(3)	83(2)
C(43)	2500(3)	6622(2)	5235(3)	82(2)	3942(4)	1693(2)	5135(3)	106(2)
C(44)	1522(3)	6718(2)	4666(4)	87(2)	4968(3)	1720(2)	4688(4)	100(2)
C(45)	1176(3)	6457(2)	3394(3)	74(2)	5033(3)	1501(2)	3417(4)	83(2)
C(46)	1814(2)	6103(2)	2716(3)	58(1)	4037(3)	1235(2)	2621(3)	64(1)
C(51)	4465(2)	5929(2)	-358(3)	53(1)	1326(2)	1170(2)	-773(3)	53(1)
C(52)	4339(3)	6209(2)	-1579(3)	66(1)	1777(3)	1397(2)	-1955(3)	62(1)
C(53)	5247(3)	6737(2)	-2057(3)	79(2)	1539(3)	1986(2)	-2551(3)	77(2)
C(54)	6292(3)	6984(2)	-1364(3)	80(2)	845(3)	2348(2)	-2001(3)	83(2)
C(55)	6433(3)	6698(2)	-179(3)	75(2)	369(3)	2115(2)	-850(3)	80(2)
C(56)	5530(3)	6171(2)	327(3)	64(1)	607(3)	1529(2)	-230(3)	65(1)
C(311)	24(3)	2968(2)	2323(3)	65(1)	3135(3)	-1806(2)	1997(3)	68(1)
C(312)	-1047(3)	2457(2)	2073(3)	74(2)	3845(3)	-2237(2)	1727(3)	78(2)
C(313)	-1900(3)	2647(2)	1372(3)	75(2)	4894(3)	-1926(2)	1269(3)	75(2)
C(314)	-1689(3)	3353(2)	934(3)	73(2)	5237(3)	-1184(2)	1072(3)	82(2)
C(315)	-627(3)	3864(2)	1170(3)	65(1)	4538(3)	-751(2)	1308(3)	68(1)
C(321)	2979(3)	4221(2)	3748(3)	71(2)	1194(3)	-631(2)	3527(3)	62(1)
C(322)	3426(3)	4249(2)	5015(3)	89(2)	817(3)	-646(2)	4772(3)	78(2)
C(323)	2793(3)	4361(2)	6014(3)	93(2)	1572(3)	-581(2)	5820(3)	85(2)
C(324)	1723(3)	4434(2)	5772(3)	82(2)	2705(3)	-514(2)	5654(3)	84(2)
C(325)	1249(3)	4378(2)	4507(3)	66(1)	3085(3)	-526(2)	4416(3)	69(2)

Table 5. Atomic co-ordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) of compound **11**. Equivalent isotropic U is defined as $\frac{1}{3}$ of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
C(1)	1608(1)	6983(3)	-53(3)	36(1)
C(2)	1405(1)	6519(3)	-1453(3)	47(1)
O(3)	1543(1)	5211(2)	-1598(2)	51(1)
C(4)	1821(1)	4760(3)	-436(3)	44(1)
C(5)	2013(1)	5913(3)	454(3)	35(1)
S(6)	1805(1)	8716(1)	-61(1)	48(1)
C(7)	1156(1)	8654(3)	804(3)	38(1)
C(8)	1108(1)	7336(3)	818(3)	34(1)
C(9)	704(1)	6342(3)	1231(3)	36(1)
O(20)	1160(1)	7073(3)	-2339(2)	69(1)
O(40)	1908(1)	3630(2)	-302(2)	60(1)
C(71)	824(1)	9802(3)	1131(3)	40(1)
C(72)	284(1)	9714(3)	1629(3)	48(1)
C(73)	-29(1)	821(4)	1831(4)	54(1)
C(74)	187(2)	2035(3)	1522(4)	58(1)
C(75)	713(2)	2125(3)	1018(4)	67(1)
C(76)	1037(1)	1034(3)	821(4)	57(1)
O(90)	681(1)	5356(2)	519(2)	49(1)
C(91)	370(1)	6492(3)	2489(3)	37(1)
C(92)	587(1)	7132(3)	3626(3)	46(1)
C(93)	280(2)	7207(4)	4814(3)	59(1)
C(94)	-241(2)	6661(4)	4854(4)	64(1)
C(95)	-459(1)	6024(4)	3715(4)	62(1)
C(96)	-154(1)	5932(3)	2534(3)	47(1)
C(501)	1984(1)	5689(3)	1998(3)	36(1)
C(502)	1763(1)	4575(3)	2580(3)	44(1)
C(503)	1727(1)	4446(4)	3996(3)	53(1)
C(504)	1907(1)	5445(4)	4835(3)	59(1)
C(505)	2126(2)	6557(4)	4278(3)	59(1)
C(506)	2172(1)	6676(3)	2865(3)	48(1)
C(507)	2617(1)	6100(3)	-40(3)	38(1)
C(508)	2733(1)	6707(3)	-1283(3)	50(1)
C(509)	3270(2)	6739(4)	-1785(4)	59(1)
C(510)	3695(1)	6153(4)	-1065(4)	64(1)
C(511)	3585(2)	5552(4)	165(4)	68(1)
C(512)	3053(1)	5520(4)	669(4)	54(1)

Table 6. Atomic co-ordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) of compound 9a. Equivalent isotropic U is defined as $\frac{1}{3}$ of the trace of the orthogonalised tensor.

	x	y	z	U(eq)
C(1)	2244(2)	7667(2)	946(2)	56(1)
N(2)	2228(1)	7260(2)	2028(2)	61(1)
C(3)	1972(2)	6493(2)	1645(3)	64(1)
O(3)	1799(1)	5854(1)	2121(2)	86(1)
C(4)	2017(2)	6749(2)	438(3)	60(1)
C(5)	1643(2)	8348(2)	824(2)	58(1)
O(5)	1025(1)	8305(1)	1141(2)	73(1)
N(6)	1944(1)	9041(2)	305(2)	58(1)
C(7)	2712(1)	8911(2)	235(2)	55(1)
C(8)	2914(2)	8127(2)	584(2)	55(1)
C(9)	2332(2)	7621(2)	3086(3)	61(1)
C(10)	2150(2)	7170(2)	4001(3)	77(1)
C(11)	2261(2)	7525(3)	5019(3)	92(2)
C(12)	2563(2)	8318(3)	5167(3)	88(2)
C(13)	2737(2)	8753(2)	4251(3)	88(2)
C(14)	2627(2)	8420(2)	3212(3)	76(1)
C(15)	2685(2)	8696(3)	6282(3)	129(2)
C(16)	1298(2)	6720(2)	-212(3)	69(1)
C(17)	1138(2)	7285(2)	-1066(3)	83(2)
C(18)	463(2)	7257(3)	-1662(3)	99(2)
C(19)	-43(2)	6671(3)	-1402(4)	125(2)
C(20)	111(3)	6126(3)	-576(4)	137(3)
C(21)	774(2)	6136(3)	11(3)	103(2)
C(22)	2636(2)	6300(2)	-123(3)	69(1)
C(23)	3132(2)	5790(2)	453(3)	89(2)
C(24)	3697(2)	5384(3)	-51(4)	112(2)
C(25)	3781(2)	5490(3)	-1141(4)	117(2)
C(26)	3302(2)	5992(3)	-1738(4)	107(2)
C(27)	2739(2)	6398(2)	-1230(3)	85(2)
C(28)	1540(2)	9826(2)	156(3)	59(1)
C(29)	1031(2)	9890(2)	-681(3)	77(1)
C(30)	594(2)	10609(3)	-796(3)	92(2)
C(31)	684(2)	11258(2)	-55(4)	94(2)
C(32)	1193(2)	11187(3)	775(4)	117(2)
C(33)	1628(2)	10469(2)	909(3)	96(2)
C(34)	3180(1)	9615(2)	-140(2)	55(1)
C(35)	3756(2)	9897(2)	528(3)	65(1)
C(36)	4228(2)	10517(2)	175(3)	80(1)
C(37)	4132(2)	10837(2)	-861(3)	89(2)
C(38)	3554(2)	10568(2)	-1533(3)	85(2)
C(39)	3071(2)	9967(2)	-1167(3)	69(1)
O(40)	3835(1)	7468(2)	1635(2)	82(1)
C(40)	3661(2)	7757(2)	736(3)	61(1)
C(41)	4169(2)	7688(2)	-182(3)	65(1)
C(42)	4834(2)	7266(2)	23(3)	87(2)
C(43)	5302(2)	7159(3)	-810(4)	117(2)
C(44)	5156(2)	7460(3)	-1828(4)	121(2)
C(45)	4495(2)	7880(3)	-2044(3)	108(2)
C(46)	4009(2)	7981(2)	-1210(3)	80(1)

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