Pergamon

Tetrahedron 55 (1999) 2973–2984

TETRAHEDRON

Regio – and Stereoselective Photocycloadditions of Heterocyclic 2,3-Diones - Evidence for an Unexpected 1, 2 - Aroyl Migration [1]

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Received 20 November 1998; accepted 18 January 1999

Abstract : Photocyclization of the heterocyclic 2,3-diones **1a-d** with electron rich alkenes affords regio- and stereoselectively the 2+2 adducts **2**, from **1b** with benzophenone as photosensitizer also the Paterno-Büchi adduct **3** is obtained. Similarly, with phenylethyne the cycloadducts **4** are formed in moderate to low yields, in case of **1c** the azepinone **6** is the only reaction product. Thermolysis of **4a** generates the pyrono compound **5**. Irradiation of the N-arylpyrrolediones **1e, f** and ethylvinyl ether give furo[3,2-c]pyrrolones **7** thus making evident an unexpected 1,2-benzoyl migration. Structural elucidation of all ring systems described is based upon X-ray analyses of **2d**, **5** and **7f**, respectively.

Keywords : [2+2]photocycloadditions, heterocyclic 2,3-diones, 1,2-aroyl migration, X-ray analyses

Introduction

The oxa-1,3-diene moieties in heterocyclic 2,3-diones **1** are well known to add isocyanides [2, 3], several heterocumulenes [4,5, 6] and electron rich alkenes [7] via formal [4 + 1] or [4 + 2] cycloaddition processes affording various mono- and bicyclic heterocyclic systems. Their molecular skeletons were determined by single-crystal X-ray diffraction analyses and ^{1}H- as well as ^{13}C NMR measurements. [2, 3, 4, 5, 6, 7] The primary formed cyclo-adducts in most cases are not stable and undergo unusual furandione rearrangements, made evident by ^{17}O-labeling experiments. [1, 8, 9] In contrast, these 2,3-diones **1** have been found to undergo photochemically and thermaly initiated [2+2] cycloaddition reactions to diphenylketene and diphenylketene-*N*-(4-methylphenyl) imine via their 3-carbonyl group thus leading to rearranged cycloadducts as well as [2+2] cycloreversion products [10]. In order to further explore the chemistry of those heterocyclic 2,3-diones , in particular, to examine their photochemical behaviour in more detail regarding the multifunctionality present (cyclic enone systems with additional carbonyl groups) and considering the results observed with ketene derivatives [10], photocycloaddition reactions now employing electron rich alkenes and phenylethyne were investigated.

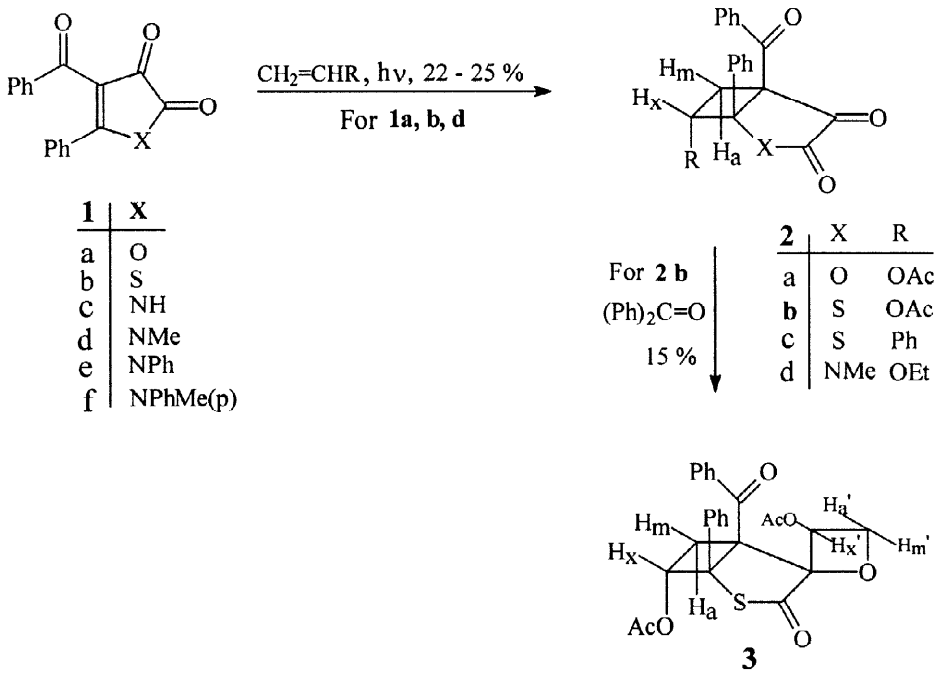
Results and Discussion

Photocyclization of the 2,3-diones **1a,b, d** with electron rich alkenes (ethylvinyl ether, vinyl acetate, styrene), initiated by irradiation with aid of a Hg - high pressure lamp (150W, no wave-length selection , pyrex apparatus), affords the 2+2 adducts **2** as the main reaction products (22-25%) isolated, obviously the result of a cycloaddition process of the alkene across the endocyclic C=C of the oxa-1,3-diene system (= „enone"). The regioselectivity observed (head-to-tail addition) corresponds well to the general findings that electron-deficient alkenes react with triplet enones to yield head-to-head adducts, while electron-rich alkenes lead to head-to-tail

Dedicated with best wishes to Professor Henk van der Plas, Agricultural University, Wageningen, The Netherlands, on the occasion of his 70th birthday.

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00078-2

adducts. [11, 12, 13, 14, 15] Various reasonable explanations for that predictable regioselectivity have been given involving either a n,π* excited enone triplet [16] or an enone π,π* triplet as reactive state. [17, 18, 19, 20] Then the polarity of the alkene directs the attack of the triplet and thus determines the regioselectivity of the reaction. [21] Also an 1,4-biradical intermediate should play an important role. [22, 23] Photocycloaddition reactions of enone systems in general are one of the most widely explored topics in photochemical reactions. A rough selection of review papers dealing with synthetic and mechanistic aspects within that field is given . [14, 24, 25, 26, 27, 28]



1	X
a	O
b	S
c	NH
d	NMe
e	NPh
f	NPhMe(p)

2	X	R
a	O	OAc
b	S	OAc
c	S	Ph
d	NMe	OEt

3

Scheme 1

The regiochemistry as well as the ENDO conformation of adducts **2** can be deduced from ^{1}H- NMR - and long-range coupling data in the ^{13}C NMR spectra. (details see Experimental Part). For **2a** in particular, the bridge-head carbons C-3a (62.8, t, ^2J= 4.5Hz) and C-5a (86.4, m) are clearly assigned from their chemical shift values and the corresponding coupling pattern. Coupling constants of the AMX spin system exhibit dieder angles of 10° (H_m, H_x) and 130° (H_a, H_x), respectively, which also support the ENDO position of the OAc group. IR absorption bands at 1800 and 1750 cm^{-1} indicate that the furan-2,3-dione moiety is still present. The regio- and stereochemistry of the thiophenedione adducts **2b,c** again have been assigned from ^{1}H- and ^{13}C NMR data (details see Experimental Part). In addition, a steady state-NOE experiment with **2c** exhibited the correct regiochemistry : Irradiation of the o-protons of the benzoyl ring (δ = 7.64, 7.61 ppm) resulted in a response at the protons at C-4 (δ = 2.73, 3.83 ppm) only! Furthermore, the stereochemistry of **2** in general is confirmed by an X-ray study of **2d** again indicating a *cis*-addition of the two reactants leading to an ENDO position of the EtO substituent (Figure 1). **2d** crystallizes with DME in a molar ratio of 2 : 1, the unit cell contains Z = 2 molecules of **2d** and 1 molecule dimethoxyethane. Identical coupling constants ($^3J_{H,H}$ = 7.5 Hz) for the AMX – system in **2d** are the result of dieder angles of 140° (H_a, H_x) and 20° (H_m, H_x), respectively.

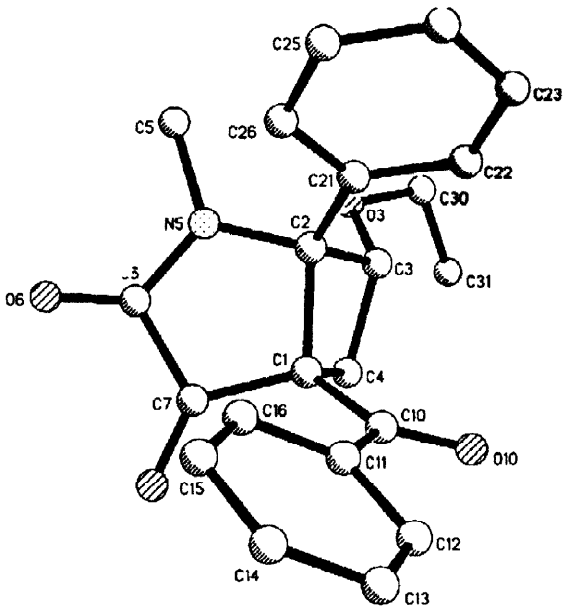


Figure 1. Perspective drawing of the molecule **2d** without H atoms. Hatched circles represent oxygen atoms, the dotted circle the nitrogen atom, respectively.

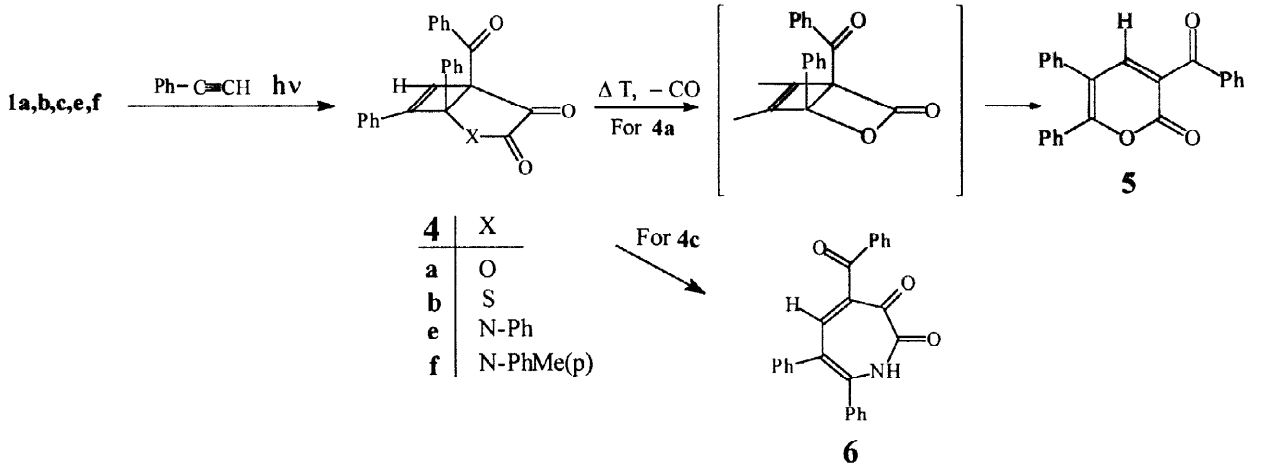
Similar 2+2 photocycloadditions employing various substituted pyrroldiones, analogues of **2d,** have been observed and described by Sano, Tsuda et al. [29, 30, 31, 32, 33, 34].

When **1b** is treated with vinyl acetate in the presence of benzophenone as a common photosensitizer , [35, 36] an additional Paterno-Büchi reaction [25, 37, 38] across the C=O at C-3 of **2b** has been observed affording the double 2+2 adduct **3**. The exact stereochemistry of **3** has been obtained from a steady state - NOE experiment : Based upon the *syn*-position of the phenyl and benzoyl groups at C-3a and C-5a, respectively , irradiation of $H_{a'}$ leads to a respond of $H_{m'}$ and the benzoyl protons at 7.92 and 7.88 ppm as well; $H_{m'}$ effects $H_{x'}$ and $H_{a'}$, while $H_{x'}$ only interacts with $H_{m'}$. These results make evident $H_{a'}$ to be oriented towards the benzoyl ring and *trans* to $H_{x'}$. This regiochemistry found agrees well with the polarization of the C=O group in its n, π^*- excited state [25] and is also observed e.g.with photoreactions on to 4,6-dimethylbenzofuran-2,3-dione. [39]

The 2,3-diones **1a,b,e,f** and phenylethyne combine under identical photochemical conditions regioselectively to afford the corresponding 2+2 cycloadducts **4a,b,e,f** in yields of 20-40%, again indicating a head-to-tail orientation of the reactants during ring closure, although 1-alkynes have been reported to give head-to-head photoadducts with cyclopentenone and cyclohexenone, respectively. [40] Employing **1c**, the primary 2+2 adduct obviously is not stable and rearranges into the azepindione derivative **6** as a result of a valence isomerization process. Similar ring enlargement reactions of related systems are known in principle, but usually proceed not simultaneously but under thermolysis [41, 42] or alkaline catalysis. [43, 44, 45] In order to verify the regiochemistry of **4** long-range couplings from ^{13}C NMR data were helpful, in particular to assign the sp^3 – carbons C-3a and C-5a, respectively (e.g. **4a** : C-3a 69.4 (d, $^2J_{CH}$ = 3 Hz); C-5a 88.0 ppm (dt, $^3J_{CH}$ = 14Hz, 4.5Hz).

In addition, when **4a** is refluxed in toluene, the pyrone **5** is obtained in 84% yield. Obviously after extrusion of carbon monoxide the primary formed cyclobuta[b]oxetan-2-one intermediate undergoes electrocyclic ring

opening to give **5**, but no decarboxylation reaction leading to the corresponding cyclobutadiene derivative could be observed. [46]



Scheme 2

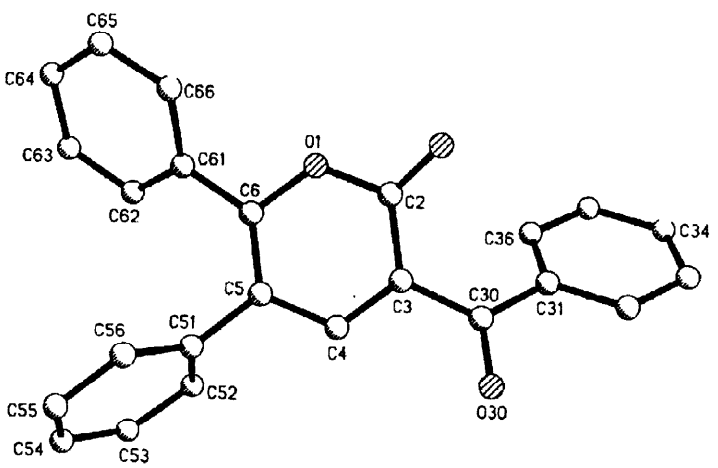
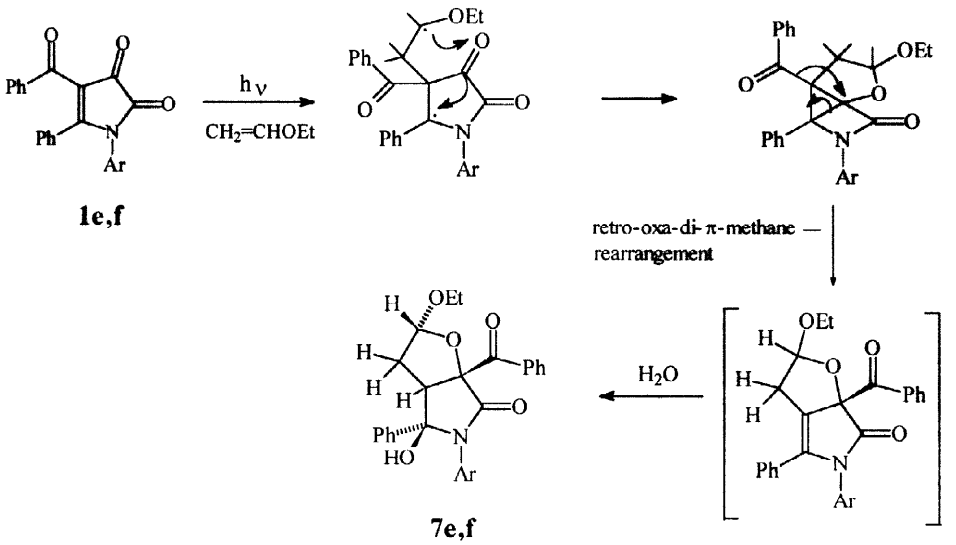


Figure 2. - Perspective drawing of the molecule **5**. Hatched circles represent oxygen atoms.

Much to our surprise, a completely divergent result was found from the photocycloaddition of the *N*-aryl-pyrroldiones **1e,f** and ethylvinyl ether : The reaction products **7e, f** were isolated from the crude reaction mixture as the only crystalline compounds in rather low yields (16%, 15%, respectively). Their structure could clearly be elucidated with aid of an X-ray single crystal analysis of **7f**, indicating the presence of a furo[3,2-c]pyrrolone ring system as the result of a novel and unexpected 1,2-migration of the benzoyl moiety (Figure 3). The X-ray analysis of **7f** makes the assigment of ^{1}H - as well as ^{13}C - NMR data easy (ring carbons only): δ = 166.3 (lactam carbonyl, d, ^{3}J = 4.8 Hz), 101.9 (C-2, d, ^{1}J=165 Hz), 91.7 (C-4, d, ^{2}J= 7.5 Hz), 90.6 (C-6a, m), 53.3 (C-3a, d, ^{1}J= 132 Hz), 33.3 ppm (C-3, t, ^{1}J= 130 Hz). In the ^{1}H NMR spectrum, besides the aromatic and the OEt-protons, the OH is found at 6.1 ppm (exchangeable with D_2O) while the remaining protons form an BMX spin system at 5.20 (d, 5Hz), 3.20 (dd, 16Hz, 4Hz), 1.97 (td, 16 Hz, 5Hz),



Scheme 3

1.70 ppm (dd, 16Hz, 4Hz). A reasonable reaction pathway for that unusual conversion is outlined in Scheme 3 : The primary formed biradical does not cyclize to give the 2+2 adduct as usually observed (see compounds **2**) but via attack to the carbonyl oxygen at C-3 could be stabilized by forming a tricyclic intermediate. Similar tricyclic systems consisting of condensed three-, four- and five-membered rings have already been prepared. [47, 48] The reaction should now proceed further via an uncommon retro-oxa-di-π-methane rearrangement [25, 49, 50, 51] which would explain the formation of the furo[3,2-c]pyrrole skeleton as well as the surprising 1,2-aroyl shift observed. While 1,3- and even 1,5-acyl migrations („photo-Fries rearrangement") are quite common [52, 53] as to our knowledge no photochemical initiated 1,2-carbonyl shifts have been found so far. However, there are a few 1,2-carbonyl migrations under quite different reaction conditions (strongly acidic or basic media) described.[54, 55, 56] Finally, addition of water through work-up affords **7** as the stable final product.

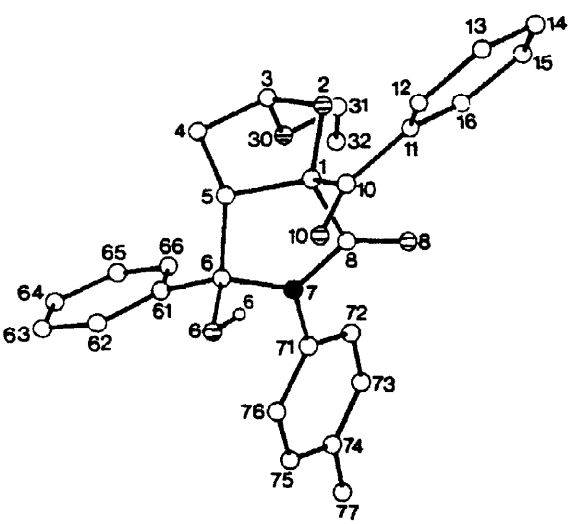


Figure 3. Perspective drawing of the molecule **7f**. Hatched circles are oxygen atoms, the black circle is the nitrogen atom.

Experimental

Melting points were determined on a Tottoli Apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^{1}H- and ^{13}C NMR spectra were recorded at 200 MHz and 50MHz, respectively, on a Varian XL 200 instrument, TMS as internal standard. Microanalyses were performed on a C,H,N Automat Carlo Erba 1106. Irradiation was performed using a 150 W Hanau TQ 150 high-pressure mercury lamp under permanent cooling in a Cryomat Haake EK 50 keeping 5°C – 10°C inside the reaction vessel. Solvents were dried according to standard procedures.

The 2,3-diones **1a,e,f** were prepared according to the literature, [57, 58] the thiophen-2,3-dione **1b** [59] and the pyrrol-2,3-diones **1c,d** [59, 60] were synthesized by modified procedures (see below). Ethylvinyl ether, vinyl acetate, styrene and phenylethyne were purchased and used without further purification.

4-Benzoyl-2,3-dihydro-5-phenyl-thiophene-2,3-dione (**1b**) [59] : When dry gaseous hydrogen sulfide was bubbled through a solution of 0.5g of **1a** in toluene for 0.5 h, the colour of the solution changes from pale yellow to orange. Keeping the reaction mixture over night at 20°C and evaporating the solvent at 40°C affords an oily residue which slowly crystallizes. Triturating with dry ether gives 0.35g **1b** (70%) of an orange solid, mp 102°C (ref. [59]: mp 102°C).

4-Benzoyl-2,3-dihydro-1H-5-phenylpyrrole-2,3-dione (**1c**) [59]: Gaseous ammonia, dried over potassium hydroxide, is run into 100 ml of dry toluene for 15 min. Then 4.6g of **1a** is added and the solution is kept at 20° for 2 h with stirring until a colourless solid precipitates. After suction, when the crude product is boiled in 20 ml of acetic acid for 5 min, the colour of the solution turns to deep red. By cooling 3.0g **1c** (73%) of an orange product crystallizes, mp 174°C (ref. [59]: 175°C).

4-Benzoyl-2,3-dihydro-1-methyl-5-phenylpyrrole-2,3-dione (**1d**) [60]: a) Gaseous methylamine is bubbled through 50 ml of dry toluene for 20 min, then 2.5g of **1a** are added and the reaction mixture is stirred at 20°C for 1h until a colourless precipitate (3g, 98%) is isolated and identified as the corresponding open-chain 3-benzoyl-2,4-dihydroxy-1-methyl-4-methylamino-4-phenyl-crotonic acid amide : mp 125-127°C; IR(KBr): 3600-2400 (b, OH, NH); 1685, 1660 cm^{-1} (C=O); ^{13}C NMR (DMSO-d_6): δ = 88.7, 114.8, 164.0, 166.6, 185.6 ppm; Anal. calcd. for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: C, 67.30; H, 6.10; N, 8.13.
b) 3g of the crotonic acid amide derivative obtained above (a) is suspended in 15 ml of acetic acid and heated under reflux for 5 min until the reaction mixture has turned into a deep red solution. After cooling to 20°C 5 ml of ether are added and the red precipitate is filtered off and dried. Yield : 1.5g **1d** (58%), mp 199°C (ref. [60]: mp 198-199°C).

rel-(3aS,5R,5aS)-5-Acetyl-3a-benzoyl-3a,4,5,5a-tetrahydro-5a-phenyl-cyclobuta[b]furan-2,3-dione (**2a**) : A solution of 1g of **1a** and 0.3g benzophenone in 100 ml vinylacetate is irradiated for 1.5 h at 10°C. After evaporation an oily residue is obtained, dissolved in ether and by addition of petroleum ether (40-60°C) a crude, amorphous precipitate is formed, filtered off and again is treated with ether/petroleum ether. This procedure is repeated twice until the amorphous residue turns into a crystalline solid which then is recrystallized from cyclohexane to give 0.35g **2a** (21%) pure product; mp : 167-169°C; IR(KBr): 1800, 1750,

1675 cm^{-1} (C=O); ^1H NMR($CDCl_3$): 2.5 (dd, H_a (J_{am}= 14.0 Hz, J_{ax}= 4.0 Hz)), 3.95 (dd, H_m (J_{mx}= 8.0 Hz)), 5.45 (dd, H_x); ^{13}C NMR(DMSO-d_6, ring carbons only): 158.2 (s, C-2), 188.7 (s, C-3), 86.4 (m, C-5a), 73.0 (dd,J_1=160 Hz, J_2= 4.0 Hz, C-5), 62.8 (t, ^2J= 4.5 Hz, C-3a), 31.0 (t, J_1= 140 Hz); Anal. calc. for $C_{21}H_{16}O_6$: C, 69.23; H, 4.43; Found : C, 69.49; H 4.47.

rel-(3aS, 5R, 5aS)-5-Acetyl-3a-benzoyl-3a,4,5,5a-tetrahydro-5a-phenyl-cyclobuta[b]thiophene-2,3-dione (**2b**) : 0.7g **1b**, dissolved in 100 ml of vinylacetate, are irradiated at 17°C for 45 min. After evaporation the residue is dissolved in ether and after 3 d a yellow precipitate is formed and recrystallized from n-BuOH to give 0.26g (23%) of **2b**; mp : 138-140°C; IR (KBr) : 1735, 1700, 1670 cm^{-1} (C=O); ^1H NMR($CDCl_3$): 2.10 (s, Me) 2.46 (dd, H_a (J_{am}= 14.0 Hz, J_{ax} = 6 Hz)), 3.97 (dd, H_m (J_{am}= 14.0 Hz, J_{mx} = 8 Hz)), 5.84 (t, H_x); ^{13}C NMR($CDCl_3$): 193.6 (benzoyl-C), 191.4 (C-3),188.8 (C-2), 71.6 (C-5), 64.8 (C-3a), 60.6 (C-5a), 33.2 (C-4); Anal. calc. for $C_{21}H_{16}O_5S$: C, 66.30, H 4.24, S 8.43; Found: C, 66.14, H 4.40, S, 8.23.

rel-(3aS, 5S, 5aS)-3a-Benzoyl-3a,4,5,5a-tetrahydro-5,5a-diphenyl-cyclobuta[b]thiophene-2,3-dione (**2c**): After irradiation of 1g of **1b** and 5 ml of styrene, dissolved in 100 ml of dry acetonitrile, at 17°C for 1 h and evaporation of the solvent, the remaining residue is dissolved in ether and after 3 days affording a precipitate, recrystallized from n-BuOH 0.3g (22%) of yellow crystals **2c** were obtained; mp : 195-197°C: IR(KBr) : 1740, 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) : 2.73 (dd, H_a (J_{am} = 12 Hz, J_{ax} = 10 Hz), 3.83 (dd, H_m , J_{am}= 12 Hz, J_{xm} = 10 Hz), 5.13 (t, H_x), 7.0-7.7 (m, Aromat): ^{13}C NMR ($CDCl_3$): 194.3 (dd, C-3, ^3J=3.5 Hz, ^3J = 1.1 Hz), 192.6 (m, benzoyl-C), 188.3 (s, C-2), 65.7 (dt, C-5a, ^2J= 3 Hz, ^3J= 4.0 Hz), 62.5 (d, C-3a, ^2J= 3.5 Hz), 44.3 (d, C-5,^1J= 150 Hz), 27.6 (t, C-4, ^1J= 162 Hz); Anal. calc. for $C_{25}H_{18}O_2S$: C, 75.36, H, 4.55, S 8.05; Found : C, 75.26, H 4,62, S, 7.79.

rel-(3aS, 5R, 5aS)-3a-Benzoyl-5-ethoxy-3a,4,5,5a-tetrahydro-1-methyl-5a-phenyl-cyclobuta[b]pyrrole-2,3-dione (**2d**): After irradiation of 0.45g **1d** together with 1.1g ethylvinyl ether in 75 ml of dimethoxyethane (temperature: 5°C, reaction time : 2.5 h) and evaporation the oily residue is again triturated with dimethoxyethane to give 0.12g **2d** (22%) bright crystals after 2 d at 20°C; mp: 163-165°C; IR(KBr): 1760, 1720, 1655 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 1.18 (t, CH_3, ^3J= 8 Hz), 2.20 (dd, H_a, J_{ax}= 7.5 Hz, J_{am} = 13 Hz), 3.22 (s, OMe from DME), 3.42 (s, OCH_2 from DME), 3.50 (dd, H_m, J_{mx} = 7.5 Hz), 3.57 (q, OCH_2, ^3J= 8 Hz), 5.00 (t, H_x), 7.1-7.4 (m, Aromat); Anal. calc. for $C_{22}H_{21}NO_4$ x ½ DME : C, 70.57, H, 6.42, N 3.43; Found: C, 70.32, H, 6.09, N, 3.42.

rel-(3S, 3'R, 3aR, 5R, 5aS)-3-Spiro[3a-benzoyl-3',5-diacetyl-3',4'-dihydro-5a-phenyl-2'H-oxetane-3a,4,5,5a-tetrahydro-cyclobuta[b]thiophene-2-one] (**3**) : 0.7g **1b**, dissolved in 100 ml of vinylacetate, are irradiated at 7°C for 45 min in the presence of 0.28g benzophenone. Evaporation affords an oily residue which is dissolved in ether and after 3 d 0.12g (11%) of crystalline **3** are obtained, recrystallized from n-BuOH. From the etheral mother liquor also 0.06g (6%) of **2b** are isolable. **3** : mp : 206-208°C; IR(KBr) : 1750, 1700, 1675 cm^{-1} (C=O); ^1H NMR($CDCl_3$): 1.52 (s, Me), 1.70 (s, Me); 2 AMX spin systems: 2.95 (dd, H_a , J_{am}= 12.0 Hz, J_{ax} = 8.0 Hz), 3.20 (dd, H_m, J_{mx}= 8.0), 5.88 (t, H_x), 3.70 (dd, $H_{a'}$, $J_{a'm'}$ = 6.0 Hz, $J_{a'x'}$ = 4.0 Hz), 4.91 (t, $H_{m'}$, $J_{m'x'}$ = 6.0 Hz), 5.70 (dd, $H_{x'}$); ^{13}C NMR ($CDCl_3$): 19.6 (q, Me, ^1J=150 Hz), 20.4 (q, Me, ^1J=150 Hz), 34.0 (t, CH_2, ^1J= 155 Hz), 58.8 (s, C-3a), 66.8, 70.4 (d, C-5, C-3', ^1J= 172 Hz), 68.4 (m, C-5a), 74.0 (t, C-2', ^1J= 160 Hz), 96.8 (s, spiro-C-3), 168.6, 170.0(m, 2x CH_3), 195.2 (t, benzoyl-CO, ^3J= 4.0 Hz), 201.2 (s, C-2); Anal. calc. for $C_{25}H_{22}O_7S$: C, 64.37, H, 4.75, S 6.87; Found : C, 64.64, H, 4.79, S, 6.55.

3a-Benzoyl-3a,5a-dihydro-5,5a-diphenyl-cyclobuta[b]furan-2,3-dione (**4a**) : Irradiation of 1.5g **1a** and 5 ml phenylethine, dissolved in 95 ml of acetonitrile, at 17°C for 1.5 h affords, after evaporation and addition of 5 ml of ether/petrolether (1 : 4) with stirring, 0.86g **4a** (42%) analytically pure yellow crystals, mp : 159°C; IR(KBr): 1790, 1765, 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 6.85 (s, =CH), 7.0-7.5 (m, aromat); ^{13}C NMR ($CDCl_3$): 69.4 (d, C-3a, ^2J=3.0 Hz), 88.0 (dt, C-5a, $^3J_1$= 14 Hz, $^3J_2$= 4.5 Hz), 134.0 (d, C-4, ^1J=160 Hz), 154.6 (t, C-5, ^3J=4.5 Hz), 159.4 (s, C-2), 185.2 (s, C-3), 191.4 (t, benzoyl-CO, ^3J= 4.5 Hz); Anal. calc.for $C_{25}H_{16}O_4$: C, 78.94, H, 4.24; Found : C, 78.73, H, 4.50.

3a-Benzoyl-3a,5a-dihydro-5,5a-diphenyl-cyclobuta[b]thiophene-2,3-dione (**4b**) : 0.78g **1c** and 5 ml phenylethyne, dissolved in 95 ml of acetonitrile, were irradiated at 17°C for 45 min. Evaporation and triturating of the oily residue with ether (5 ml) gives 0.3g (30%) of **4b**, recrystallized from cyclohexane; mp : 142-144°C; IR(KBr): 1735, 1695, 1670 cm^{-1} (C=O); ^1H NMR($CDCl_3$) : 6.75 (s, =CH); ^{13}C NMR ($CDCl_3$): 62.2 (m, C-5a), 68.4 (d, C-3a, ^2J= 3.5 Hz), 120.6 (d, C-4 ,^1J= 195 Hz), 156.8 (m, C-5), 186.2, 187.2 (s, C-2, C-3), 191.6 (t, benzoyl-C, ^3J= 4.5 Hz); Anal. calc. for $C_{25}H_{16}O_3S$: C, 75.74, H, 4.07, S, 8.09; Found : C, 75.75, H 4.22, S, 7.88.

3a-Benzoyl-3a,5a-dihydro-1,5,5a-triphenyl-cyclobuta[b]pyrrole-2,3-dione (**4e**) : 0.8g **1e** and 5 ml of phenylethine, dissolved in 95 ml of dry toluene, afford after irradiation for 1.5 h at 17°C, evaporation of the solvent and triturating of the residue with 5 ml of ether 0.21g (20%) **4e** in analytically pure form; mp : 164-165°C; IR (KBr): 1755, 1720, 1670 cm^{-1} (C=O); Anal. calcd. for $C_{31}H_{21}NO_3$: C, 81.74, H, 4.65, N, 3.07; Found : C, 81.92, H, 4.86, N, 3.05.

3a-Benzoyl-3a,5a-dihydro-5,5a-diphenyl-1-(4-methylphenyl)-cyclobuta[b]pyrrole-2,3-dione (**4f**) : Exactly following the procedure for the preparation of **4e** 0.18g (23%) of **4f** are obtained from 0.6g **1f** and 5 ml of phenylethine; mp : 152-155°C (from n-BuOH); IR(KBr) : 1755, 1720, 1660 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) : 2.3 (s, CH_3), 6.9 (s, =CH), 7.0-7.4 (m, aromat); ^{13}C NMR (DMSO-d_6) : 70.0 (d, C-3a, ^2J= 3.0 Hz), 76.0 (dt, C-5a, ^3J= 12 Hz, 4.5 Hz), 136.4 (d, C-4,^1J= 195 Hz), 154.6 (m, C-5), 160.2 (s, C-2), 193.0 (s, C-3), 194.4 (t, benzoyl-CO, ^3J= 4.5 Hz); Anal. calcd. for $C_{32}H_{23}NO_3$: C, 81.86, H, 4.94, N, 2.98; Found : C, 81.80, H, 4.88, N, 2.90.

3-Benzoyl-5,6-diphenyl-pyran-2-one (**5**) : 0.4g of **4a**, dissolved in 25 ml of toluene, are refluxed for 4 h. Then the solvent is evaporated and the solid residue recrystallized from toluene affording 0.31g **5** (84%) yellow crystals, mp : 168-169°C; IR (KBr): 1725, 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 7.85 (s, =CH); ^{13}C NMR ($CDCl_3$): 118.0 (C-3), 124.2 (C-5), 151.0 (C-4), 159.1 (C-6), 162.0 (C-2), 191.3 (benzoyl-CO); Anal. calcd. for $C_{24}H_{16}O_3$: C, 81.80, H, 4.58 ; Found : C, 81.80, H, 4.55.

4-Benzoyl-6,7-diphenyl-azepine-2,3-(1H)-dione (**6**) : A mixture of 0.6g **1c** and 5 ml of phenylethyne in 95 ml of acetonitrile is irradiated at 15°C for 2 h. After evaporation and addition of 5 ml of ether a crude precipitate is isolated by suction, washed with dry acetone and recrystallized from n-BuOH to give 0.17g (21%) of yellow **6**, mp : 252-254°C; IR(KBr): 3175 (NH), 1700, 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 7.72 (s, =CH); ^{13}C NMR (DMSO-d_6) : 120.4 (s, C-4), 139.4 (m, C-7), 146.3 (d, C-5, ^1J= 150 Hz), 163.0 (s, C-2), 179.0 (s, C-3), 197.6 (t, benzoyl-CO, ^3J= 4.5 Hz), C-6 within the aromatic region; Anal. calcd. for $C_{25}H_{17}NO_3$: C, 79.14, H, 4.52, N, 3.69; Found : C, 79.31, H, 4.54, N, 3.78.

Table 1. Crystal parameters for the X-ray diffraction study [61] of compounds **2d**, **5** and **7f**

Compound	2d	5	7f
Formula	$C_{22}H_{21}NO_5$ + ½ DME	$C_{24}H_{16}O_3$	$C_{28}H_{27}NO_5$
Molecular mass	408.47	352.93	457.53
a [pm]	953.2 (3)	1364.9(7)	1127.7(6)
b [pm]	1363.9(4)	558.7(3)	1547.3(3)
c [pm]	935.0 (3)	2440(1)	754.0(4)
α [deg]	94.78 (3)		103.32(3)
ß [deg]	114.31(3)	101.89(4)	96.45(4)
γ [deg]	101.16(3)		107.58(3)
V [$pm^3.10^{-6}$]	1068.5(7)	1821(2)	1196.7(9)
Z	2	4	2
d(calc)[$g.cm^{-3}$]	1.269	1.258	1.270
crystal system	triclinic	monoclinic	triclinic
space group	P-1	$P2_1/c$	P-1
diffractometer	Nicolet R3m/V	Nicolet R3m/V	Nicolet P3
radiation	MoK_α	MoK_α	MoK_α
monochromator	graphite	graphite	graphite
crystal size [mm]	0.9x1.3x0.4	0.35x0.85x0.15	0.7x0.7x0.2
data collection mode	Wyckoff-scan	Wyckoff-scan	ω - scan
theta range [deg]	1.75 – 25.0	1.75 – 25.0	1.75 – 27.5
recip.latt.segment	h = -11 - 10	h = 0 – 12	h = -14 - 14
	k = -17 - 17	k = 0 – 6	k = -20 - 19
	l = 0 - 12	l = -29 – 28	l = 0 – 9
no. refl.measd.	4892	3722	4756
no. unique refl.	4892	3225	4756
no. refl. F > 3σ (F)	3511	1640	4431
lin. abs. coeff. [mm^{-1}]	0.09	0.08	0.08
abs.correction	ψ - scan	Ψ - scan	ψ - scan
solution by	direct phase determ.	direct phase determ.	direct phase determ.
method of refinement	Full Matrix LSQ	Full Matrix LSQ.	Full matrix LSQ.
	Hydrogen positions of riding model with fixed isotropic U	Hydrogen positions of riding model with fixed isotropic U	Hydrogen positions of riding model with fixed isotropic U
parameter/F_o ratio	0.077	0.149	0.070
R, R_w	0.060, 0.059	0.082, 0.054	0.047, 0.049
program used	SHELXTL Plus	SHELXTL Plus	SHELTXL Plus

rel-(2S, 3aS, 4S, 6aR)-6a-Benzoyl-2-ethoxy-2,3-dihydro-4-hydroxy-4,5-diphenyl-6aH-furo[3,2-c]pyrrol-6(5H)-one (**7e**) : 1g of **1e** and 2.6g ethylvinyl ether, dissolved in 100 ml of dimethoxyethane, are irradiated at 10°C for 3 h. Then the solvent is removed in vacuo and the oily residue is treated with ether/petroleum ether (1 : 5) until an amorphous precipitate is formed, which is suspended in petroleum ether (b.p.40-60°C) for 2 d and again triturated with ether to afford 0.2g **7e** (16%) of a colourless compound, mp : 180-182 °C; IR (KBr) : 3380 (OH), 1715, 1665 cm^{-1} (C=O); Anal. calcd. for $C_{27}H_{24}NO_5$: C, 73.29, H, 5.47, N, 3.17; Found : C, 73.23, H, 5.50, N, 3.23.

rel-(2S, 3aS, 4S, 6aR)-6a-Benzoyl-2-ethoxy-2,3-dihydro-4-hydroxy-4-phenyl-5-(4-methylphenyl)-6aH-furo[3,2-c]pyrrol-6(5H)-one (**7f**): 1g of **1f** and 2.6g ethylvinyl ether , dissolved in 75 ml of dimethoxyethane , are irradiated at 10°C for 5 h. After evaporation and treating the oily residue with 10 ml of ether, 0.1 g of starting material **1f** has been recovered. From the etheral solution after addition of petroleum ether (b.p.40-60°C) a colourless precipitate is obtained, which is purified by treatment with ether to give 0.2g **7f** (15%) analytically pure product, mp : 180-183°C; IR(KBr): 3420 (OH), 1710, 1665 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): 1.20 (t, CH_3, ^3J=6.6 Hz), 2.17 (s, CH_3), 3.58, 4.20 (2 x m, OCH_2), 6.1(s, OH, exchangeable with D_2O), AMBX spin system : 1.70 (dd, H_a , J_{ab} = 13.5Hz, J_{am} = 3.5Hz), 1.97 (dt, H_b , J_{bx} = 5.3 Hz), 3.20 (dd, H_m , $J_{b,m}$ = 12 Hz), 5.2 (d, H_x, J_{bx} = 5.3 Hz), 7.0-8.4 (m, aromat); ^{13}C NMR (DMSO-d_6) : 17.0 (q, CH_3, ^1J = 117 Hz), 19.5 (q, CH_3, ^1J= 117 Hz), 33.3 (t, CH_2, ^1J = 132 Hz), 53.3 (d, CH, ^1J = 140 Hz), 60.0 (t, OCH_2, ^1J = 140 Hz), 90.6 (m, C-4), 91.7 (d, C-6a, ^3J= 7.5 Hz), 101.9 (d, C-2, ^1J = 165 Hz), 166.3 (d, C-6, ^3J = 4.8 Hz), 192.3 (t, benzoyl-CO, ^3J = 5.2 Hz). Anal. calcd. for $C_{28}H_{26}NO_5$: C, 73.67, H, 5.74, N, 3.07; Found : C, 73.49, H, 5.70, N, 3.02.

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