# Photoinduced diastereoselective pinacolisation of 4-oxo-4-phenylbutanamides to 4,5-dihydroxy-4,5-diphenyloctanediamides

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The photoinduced pinacolisation of 4-oxo-4-phenylbutanamides **1** afforded 4,5-dihydroxy-4,5-diphenyloctanediamides **2** and **3** with unusual diastereoselectivities up to 83%, which depends on the amide substituent. In this reaction the solvent diethyl ether acts as a hydrogen donor. The structures of pinacols **2** and **3** were confirmed by X-ray analyses. Possible reasons for the diastereoselectivity and the preferred intermolecular hydrogen abstraction from the solvent are discussed. Products **5** and **6** obtained after irradiation of 4-oxo-4-phenylbutanoic acid **4** were identified by crystal structure determination as 2,2′-diphenyltetrahydro[2,2′]bifuranyl-5,5′-diones.

## Introduction

The photoreduction of carbonyl compounds has been known for a long time. In 1900, Ciamician and Silber[1] reported one of the first procedures for the photoinduced pinacolisation of acetophenone *via* an intermolecular hydrogen abstraction from ethanol. However, when intramolecular hydrogen abstraction is possible the intermolecular hydrogen transfer is a minor reaction pathway.[2] Only a few exceptions have been reported, for instance the irradiation of 3-aminoketones with an unsubstituted alkyl chain leads exclusively to the corresponding pinacols.[3] Cyclobutyl phenyl ketone affords the appropriate diols after irradiation in propan-2-ol, however not in benzene.[4]

On our way[5] to pharmacologically interesting compounds *via* photochemical key reactions, we discovered the unexpected fact that the constitution of photoproducts formed after irradiation of amides **1** depends on the solvent used. In *tert*-butyl alcohol and dichloromethane amides **1** were observed to undergo efficient photocyclisation to δ-lactams as a result of an intramolecular hydrogen abstraction from the ε-position.[6,7] In contrast, 4,5-dihydroxy-4,5-diphenyloctanediamides **2** and **3** were obtained when the irradiation was carried out in solvents such as diethyl ether or THF. Surprisingly, these pinacols were formed with a diastereoselectivity up to 83%. Herein, we report our results for the observed ratio of inter- to intramolecular hydrogen abstraction and provide explanations for the unusual diastereoselectivity.

## Results and discussion

### Irradiation of amides 1

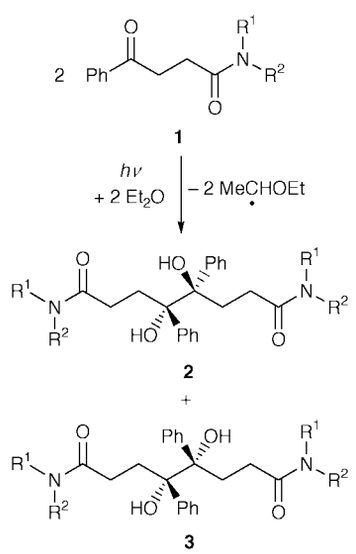
Amides **1** were irradiated in diethyl ether yielding 4,5-dihydroxy-4,5-diphenyloctanediamides **2** and **3**. Irradiation of amides **1a**–**f** gave mainly racemates **3a**–**f**, while *meso*-pinacols **2g**–**i** were formed with a slight diastereoselectivity (Table 1).

In other solvents (propan-2-ol, THF and *n*-hexane) pinacols **2** and **3** were also obtained after irradiation of reactants **1**. The yields of diamides **2** and **3** are lower in these solvents than in diethyl ether because of the formation of side products, which seem to be solvent adducts. These compounds were not isolated. The addition of solvent radicals to hydroxyl radicals has been reported for the photoreaction of ketones in diethyl ether[8] and THF.[9]

**Table 1** Yields, product ratio and diastereoselectivities of 4,5-dihydroxy-4,5-diphenyloctanediamides (**2** = *meso*-product, **3** = racemate)

| | | | Yields[a] (%) | | | |
|---|---|---|---|---|---|---|
| | $-R^1$ | $-R^2$ | **2** | **3** | **2/3** | ds (%) |
| **a** | $-(CH_2)_3-$ | | 20 | 46 | 1:2.3 | 70 (**3a**) |
| **b** | $-(CH_2)_4-$ | | 12 | 60 | 1:5 | 83 (**3b**) |
| **c** | $-(CH_2)_5-$ | | 11 | 43 | 1:3.9 | 80 (**3c**) |
| **d** | $-(CH_2)_6-$ | | 16 | 60 | 1:3.8 | 79 (**3d**) |
| **e** | $-(CH_2)_2-O-(CH_2)_2-$ | | 15 | 38 | 1:2.5 | 72 (**3e**) |
| **f** | $-CH_3$ | $-CH_3$ | 20 | 42 | 1:2.1 | 68 (**3f**) |
| **g** | $-CH_3$ | –Ph | 52 | 33 | 1.6:1 | 62 (**2g**) |
| **h** | $-CH_3$ | $-CH_2-Ph$ | 34 | 17 | 2:1 | 67 (**2h**) |
| **i** | –H | $-CH_2-Ph$ | 37 | 24 | 1.6:1 | 61 (**2i**) |

[a] Determined by HPLC.




### Characterisation of pinacols 2 and 3

Henning *et al.*[10] postulated a cyclopropanol-structure for the photoproducts of two 4-oxo-4-phenylbutanamides in diethyl ether, among them morpholide **1e**. Our characterisation of the obtained photoproducts **2** and **3** as octanediamides is based on the MS- and NMR-data and at least on X-ray crystal analyses.

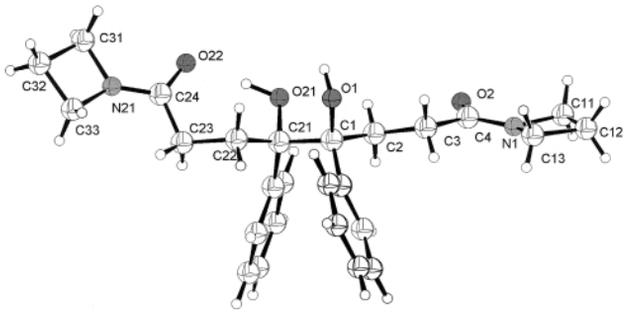



**Fig. 1** X-Ray structure of (±)-1,8-di(azetidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione **3a**.

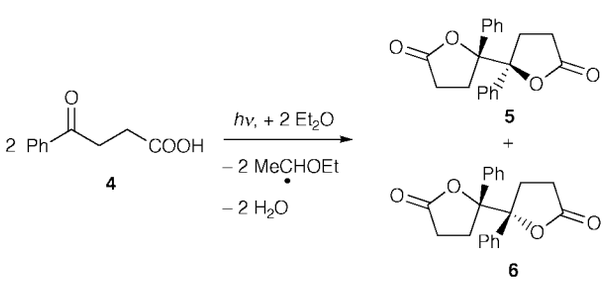
The MS-spectra of pinacols **2** and **3**, using electron impact MS, contain peaks, which correspond to ($M^+ + 1$)-peaks of the presumed cyclopropanols or ($M^+/2$)-peaks of the diamides **2** and **3**. MS-spectroscopy of compounds (**2e**, **2g** and **3e**), performed with other ionisation methods (FAB and CI), gave spectra with ($M^+ + 1$)-peaks of the pinacols.

The $^{13}$C-NMR-spectra of **2** and **3** show two $CH_2$-signals, which cannot be assigned to the amide substituents. In these spectra, there is always only one signal for the two symmetry unique carbon atoms. This fact could be explained by the pseudo-symmetric structure of pinacols **2** and **3**.

Finally, two X-ray crystal analyses confirm the pinacol-constitution of the photoproducts **2** and **3**. The crystal structure of diazetidide **3a** showed an intramolecular hydrogen bond (1.68 Å, Fig. 1). The structure of dimorpholide **3e**, which is identical with one product of Henning *et al.*,[10] was also determined by X-ray analysis. Due to distortion in the crystal, its parameters could not be fully refined, but the constitution of compound **3e** was clearly elucidated as a pinacol structure.

### Irradiation of acid 4

The synthesis of octanedioic acid derivatives by reduction of the corresponding 4-aryl-4-oxobutanoic acid derivatives is known using, for example, electrolysis[11] or irradiation.[12] In both cases the appropriate bislactones were formed *via* an intramolecular esterification of the octanedioic acids. In this context, there exist contradictory statements about the constitution of the bislactones, obtained by reduction of 4-oxo-4-phenylbutanoic acid **4**. Hasegawa *et al.*[12] described the isolated products as 4a,8a-diphenylhexahydropyrano[3,2-*b*]pyran-2,6-diones, while Price and Tomisek[13] classified the bislactones as 2,2′-diphenyltetrahydro[2,2′]bifuranyl-5,5′-diones **5** and **6**. In both cases the configurations of the obtained products were not determined.




In order to explain the diastereoselective photopinacolisation of amides **1** we were interested in irradiation of acid **4** in diethyl ether. This irradiation yielded 23% of an isolated 1 : 1 mixture of two bislactones. Their NMR data are identical with those of pyranopyrans, reported by Hasegawa *et al.*,[12] but an X-ray crystal analysis of product **6** verifies its bisfuranyl-constitution (Fig. 2) as proposed in the literature.[13] On the basis of this result we presume the bisfuranyl-constitution for the second isomer **5**.

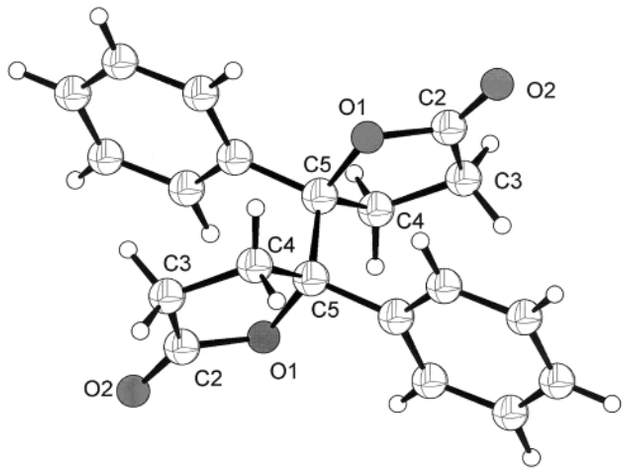
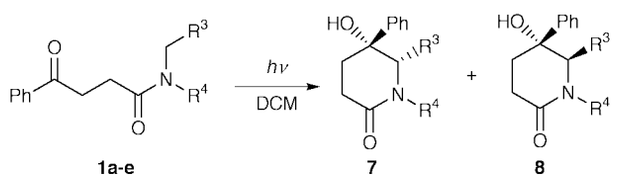



**Fig. 2** X-Ray structure of (2*RS*,2′*SR*)-2,2′-diphenyltetrahydro[2,2′]-bifuranyl-5,5′-dione **6**.

### Inter- *versus* intramolecular hydrogen abstraction

Two different classes of products were obtained after irradiation of amides **1**. The constitution of the photoproducts depends on the solvent. Diethyl ether acts as a hydrogen donor for the photopinacolisation affording diamides **2** and **3**, while in dichloromethane δ-lactams **7** and **8** are formed *via* an intramolecular hydrogen transfer.[7] This phenomenon can be




explained by the different dissociation energies of the C–H bonds in both solvents.† The energy of 99 kcal mol$^{-1}$ [14a] for homolysis of the C–H bond in dichloromethane is 7 kcal mol$^{-1}$ greater than the dissociation energy of a methylene C–H bond in diethyl ether.[15]

The nature of the hydrogen abstraction depends on the composition of the diethyl ether–dichloromethane mixture. This was shown upon the irradiation of *N*-benzyl-*N*-methyl-4-oxo-4-phenylbutanamide **1h** (Fig. 3). When irradiation was carried out in at least 20% diethyl ether the photopinacolisation was preferred.

Another reason for the preferred formation of pinacols **2** and **3** after irradiation of amides **1** in diethyl ether could be the occurrence of an initial intramolecular hydrogen abstraction from the ε-position followed by an intermolecular hydrogen transfer to the ε-position and a radical–radical combination. Dimethylamide **1f** was irradiated in [$^2H_{10}$]diethyl ether to investigate this theory. In the case of an initial occurring intramolecular hydrogen abstraction from the ε-methyl groups, a decrease in the integrals for these groups should be expected in the $^1$H-NMR spectra. Both obtained pinacols [$^2H_2$]**2f** and [$^2H_2$]**3f** do not display decreased integrals for the methyl groups.

Amides **1** differ from most other investigated alkyl aryl ketones due to their significant tendency toward photopinacolisation.[2] Compounds **1** contain an amide group as a structural peculiarity in their alkyl chain. Hence, the formation of an intramolecular hydrogen bond between the hydroxyl group in the derived radical and the amide oxygen atom is very

† n,π*-Excited ketones react similarly to alkoxy radicals. On this basis, the validity of an analogous thermodynamic relationship is assumed. Thus, $\Delta_R H^{\ddagger}$ of the intermolecular hydrogen abstraction by n,π*-excited carbonyl compounds depends on the dissociation energy of the C–H bond.[14b]

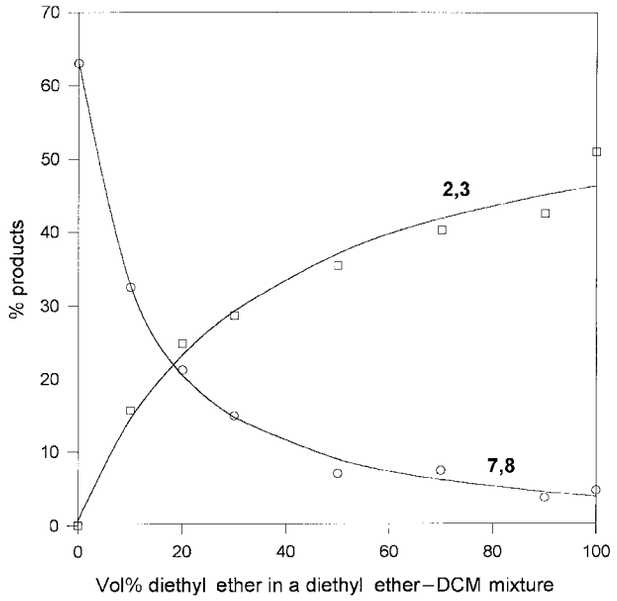



**Fig. 3** Ratio of pinacols **2** and **3** to $\delta$-lactams **7** and **8**, depending on the ratio diethyl ether to dichloromethane.

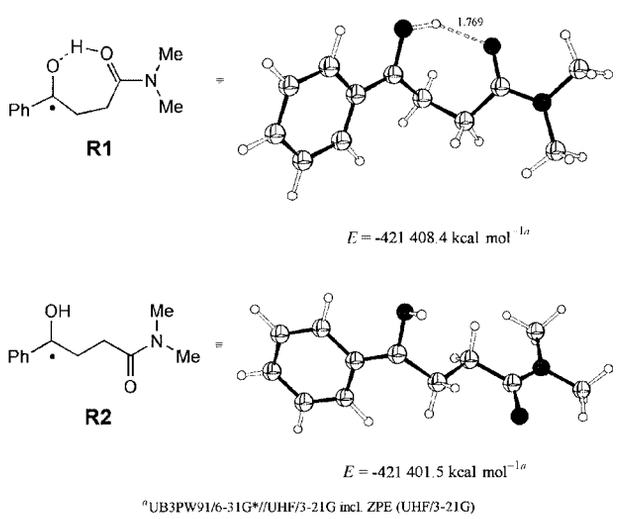



**Fig. 4** *Ab initio* calculated radical conformers **R1** and **R2**.

probable. Although the occurrence of this H-bond in the formed radical should not influence the activation barrier of the hydrogen abstraction by the excited carbonyl group, it can reduce the extent of hydrogen back transfer. It is very likely that the directly formed radical conformation after hydrogen abstraction represents a very flat minimum, which is separated from the global minimum by a very small activation barrier. Thus, by a rapid conformational equilibration of the radical the transferred hydrogen atom would be fixed and therefore difficult to transfer back to the solvent radical. Consequently, the intramolecular H-bond should increase the efficacy of the intermolecular hydrogen abstraction. A similiar behaviour is known for the analogous hydroxyl biradicals.[16] In those cases the quantum yields of decay are increased by solvents that are able to form hydrogen bonds with the hydroxyl group of the biradicals.

In order to prove the influence of an intramolecular H-bond we have performed *ab initio* calculations of the two radical conformers **R1** and **R2**. The obtained structures and energies are depicted in Fig. 4. The intramolecular hydrogen bond (1.77 Å) in the radical **R1** lowers the energy by 6.9 kcal $mol^{-1}$ compared with the energy of radical **R2**. Stabilisation by an intramolecular hydrogen bond together with an energetic profit could be the reason for a faster intermolecular

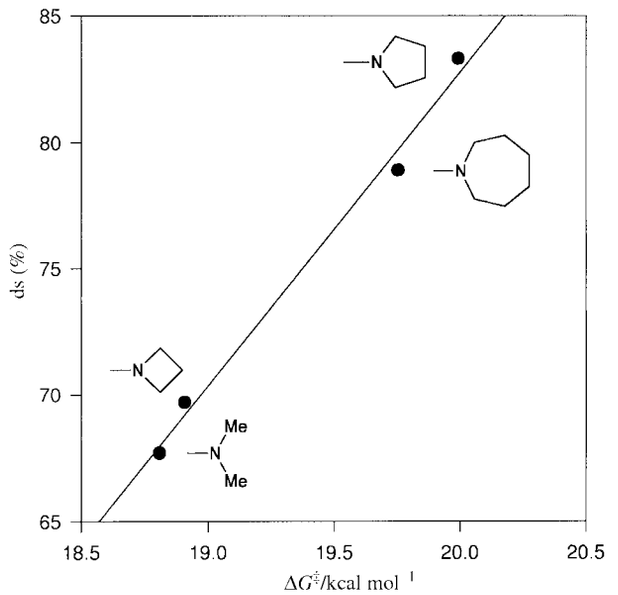



**Fig. 5** Diastereoselectivity of the formation of racemic pinacols **3**, depending on the amide rotation barrier.

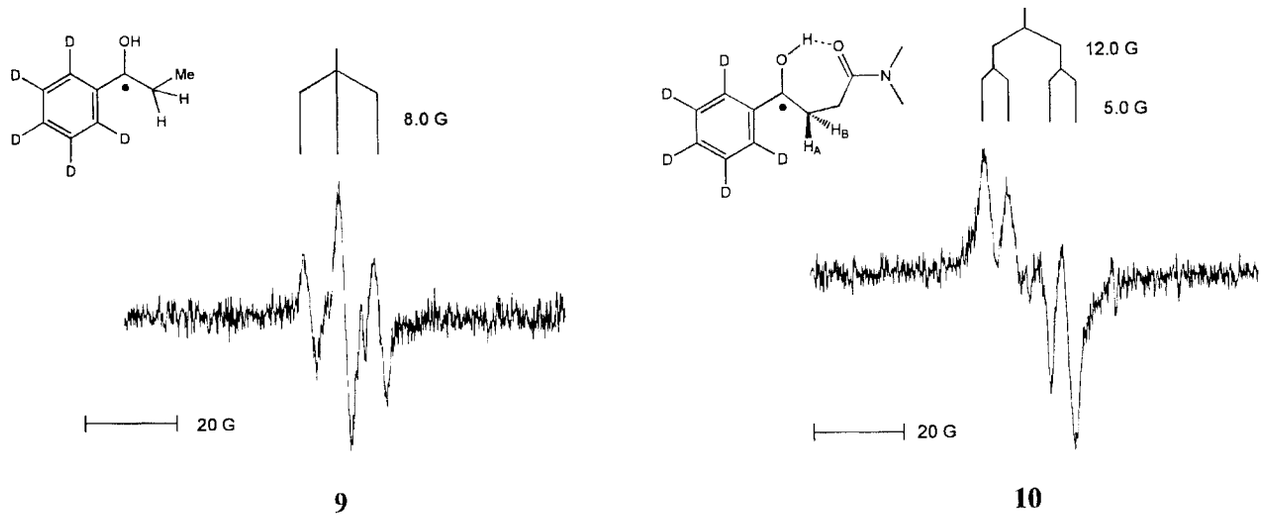
hydrogen transfer by n,π*-excited amides **1** than by other alkyl aryl ketones.

### Diastereoselectivity of photopinacolisation

Surprisingly, remarkable diastereoselectivities were observed in the photochemical reduction of amides **1** in diethyl ether. In contrast to these results irradiation of acid **4** yielded bislactones **5** and **6** as a 1:1 mixture. Because of the identical Ph–CO–$(CH_2)_2$–CO substructure in all reactants (**1** and **4**) the amide substituents must be responsible for this phenomenon. The investigated amides **1** could be classified as a) conformationally rigid amides **1a**–**f** (see Table 1, upper part) and b) amides **1g**–**i** with conformationally flexible amide substituents (Table 1, lower part). Irradiation of amides **1a**–**f** with a conformationally rigid amide residue yielded mainly the racemic pinacols **3a**–**f**, while the photoreduction of reactants **1g**–**i** with conformationally flexible substituents afforded especially the *meso*-products **2g**–**i**.

On the way to an explanation for the unexpected dependence of diastereoselectivity on the nature of the amide substituents the activation barriers $\Delta G^{\ddagger}$ of internal amide rotation were determined by dynamic NMR studies according to the literature.[17] We found a correlation between the diastereoselectivity ds of racemic pinacols **3**, resulting from the irradiation of conformationally rigid amides **1a**, **1b**, **1d** and **1f**, and the rotation energies $\Delta G^{\ddagger}$ of their amide groups (Fig. 5).

The intramolecular hydrogen bond in the radical (see above) should influence the diastereoselectivity due to the rigid 7-membered chelate ring, which has a steric and/or energetic effect on the radical–radical combination. In this case, the two hydrogen atoms at the carbon atom, which is adjacent to the radical centre, should be non-equivalent. The EPR-spectra of the radicals derived from **1g** with a conformationally rigid amide substituent and from amide **1b** with a flexible amide residue are identical. These spectra contain many lines caused by the eight protons near the radical centre and prevent an analysis of the obtained spectra. To simplify the EPR-spectra we investigated the 4-oxo-4-pentadeuterophenylbutanamide [$^2H_5$]**1g** and for comparison ethyl pentadeuterophenyl ketone. The obtained EPR-spectrum of radical **9** exhibits a coupling constant of 8.0 G (Fig. 6), which is similar to the reported value of 8.2 G.[18] In contrast, the spectrum of amide radical **10** displays two different coupling constants (5.0 G and 12.0 G, Fig. 6). They are in good agreement with the calculated[19] coupling




**9** **10**

**Fig. 6** EPR spectra of radicals **9** and **10**.

**Table 2** EPR-Data of radicals **9** and **10**

| | Observed coupling constant[a]/G | Calculated coupling constant[b]/G |
|---|---|---|
| **9** | 8.0 | — |
| **10** | 5.0 | 3.2 |
| | 12.0 | 11.1 |

[a] In some cases the 2-hydroxypropyl radical, formed from the solvent propan-2-ol, is observed with a coupling constant of 19.4 G (lit.,[18] 19.0 G). [b] UB3PW91/6-311++G**//UB3PW91/6-31G*.[19]

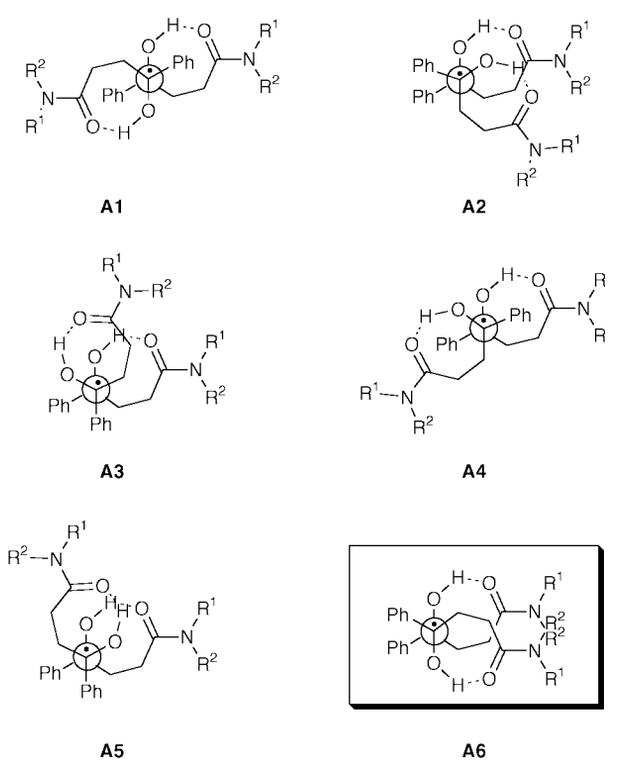



**Fig. 7** Possible geometries of radical–radical combination.

constants (Table 2). This indicates a conformationally rigidifying effect, which could be caused by an intramolecular hydrogen bond.

A slight preference for the formation of the *meso*-products was observed in a usual dimerisation of a prochiral hydroxy alkyl aryl substituted radical due to entropic reasons.[20] In the case of the dominant formation of a racemate the *meso*-products were calculated to be more stable.[20] This means that

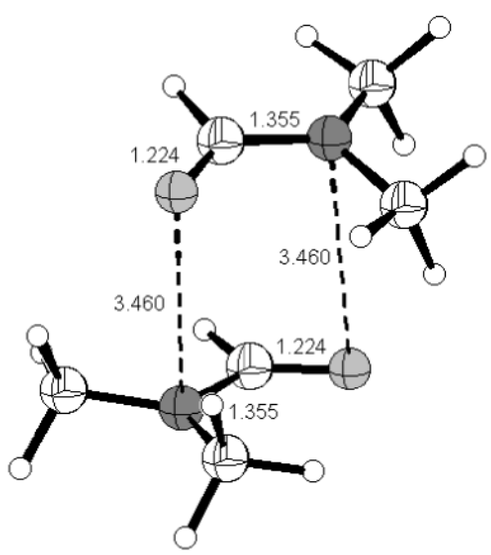



**Fig. 8** DFT calculated structure of DMF dimer.

the result of dimerisation is controlled by kinetic factors. In Fig. 7 the six possible radical–radical combination geometries of *N*,*N*-disubstituted 3-aminocarbonyl-1-hydroxy-1-phenylpropyl radicals are shown, assuming the existence of an intramolecular hydrogen bond. Conformations **A1**–**A3** lead to the *meso*-pinacols **2**, while conformations **A4**–**A6** afford the racemic products **3**. Only in geometry **A6** is an interaction between the two strong amide dipoles possible. A rotation around the amide bond and/or a substituent, which is outside the amide plane, *e.g.* benzyl or phenyl groups, disturb this interaction.

The existence of amide dimers was already proved some decades ago,[21] but to the best of our knowledge up to now no quantum chemical calculations were performed to obtain more detailed information about the geometry and the stabilisation energy of such dimers. Since the radicals derived from **1** are too large for *ab initio* calculations at a high level of theory, we chose *N*,*N*-dimethylformamide (DMF) as a model system. We found that the DMF dimer is stabilised by 7 kcal $mol^{-1}$ compared with two monomer molecules (B3PW91/6-311++G**//B3PW91/6-31G*). Furthermore, the intermolecular O–N distance amounts to 3.46 Å. Consequently, it is by nearly 2 Å longer than a C–C bond distance (Fig. 8, Table 3).

Therefore, the dipole–dipole interaction between the amide groups should begin at remarkably larger distances between the radicals than the covalent interaction between the two radical

**Table 3** Energies of DMF and its dimer

| | DMF dimer | DMF monomer |
|---|---|---|
| B3PW91/6-31G* [a,c] | −496.84269 | −248.41291 |
| ZPE [b] | 130.6 | 64.4 |
| B3PW91/6-311++G** [a,d] | −496.98569 | −248.48584 |
| $E$ [b] | −311732.9 | −311725.9 (2×) |

[a] au. [b] kcal mol$^{-1}$. [c] Geometry optimisation. [d] Single point calculation.

centres and should be responsible for a preorientation of the radicals like in **A6**.

## Conclusion

Irradiation of amides **1** affords the corresponding pinacols **2** and **3** instead of the formerly reported cyclopropanols. The dissociation energy of the C–H bond in diethyl ether causes the preferred intermolecular hydrogen abstraction in this solvent, compared with the intramolecular hydrogen transfer in dichloromethane. Additionally, an intramolecular hydrogen bond could be the reason as well for an energetic favoured intermolecular hydrogen abstraction as for the diastereoselectivity. This conformation makes an interaction between the two strong amide dipoles possible only in a radical–radical combination geometry, which yields especially the racemic pinacols **3**. Investigation of products **5** and **6**, obtained by photoinduced reduction of acid **4** in diethyl ether, confirmed the bifuryl constitution of the products.

## Experimental

### General

TLC was performed on alumina sheets with silica gel 60 $F_{254}$ (Merck), detected by UV light. Silica gel 40–63 μm (Merck) and dichloromethane–methanol (v/v) as eluent were used for flash chromatography (FC). High-pressure liquid chromatography (HPLC) was performed on an analytical SIX [$NH_2$] column (150 × 3.3 mm, 5 μm, Laboratorni Pristroje) under the following conditions: flow 1 cm$^3$ min$^{-1}$, mobile phase *n*-hexane–propan-2-ol = 95 : 5 (v/v), UV detection at 220 and 230 nm. The uncorrected melting points (mp) were determined on a Boetius micro melting point apparatus (Wagema). IR spectra were taken with a Perkin-Elmer-881 (solids as KBr pellets, oils on NaCl plates). NMR spectra were recorded with a Bruker DPX300 ($^1$H 300 MHz, $^{13}$C 75.5 MHz), using $SiMe_4$ as internal standard (0 ppm), $J$ values are given in Hz. EI-mass spectra were taken with a Hewlett Packard 5995 A, 70 eV at 293-593 K. FAB- and CI-mass spectroscopy were performed on a double-focusing VG70-250 and MAT-312 (CI with $NH_3$, FAB with xenon atoms, using nitrobenzyl alcohol as matrix and KCl as additive). EPR-spectroscopy was performed on a Bruker ESP-300 (ESP-300E software), connected with an 8″-magnet and a Bruker ER 4111VT-temperature sensor. 2-Hydroxypropyl radical is used as internal standard ($g$ = 2.0030 [18]). Conditions: modulation frequency 100 kHz, modulation amplitude 1.05 G, receiver gain 8 × 10$^5$, conversion time 163.84 ms, sweep time 167.77 s, temperature 270 K. Radicals **9** (10 db) and **10** (20 db) were formed *in situ* by irradiation in cyclohexane–propan-2-ol = 80 : 20 (v/v) with a Hanovia 977B1 1000W Hg–Xe high pressure lamp in suprasil-quartz tubes. A UG-5-filter (Schott) was used.

Amides **1a–f** and **1h–i** were synthesised as previously described.[7,22] 4-Oxo-4-pentadeuterophenylbutanamide [$^2H_5$]**1g** and ethyl pentadeuterophenyl ketone were prepared according to literature methods.[23]

### Computational details

Calculations were carried out with the *ab initio* program packages GAUSSIAN92 [24] (optimisation of radicals **R1** and **R2**) and GAUSSIAN98 [19] (calculation of the isotropic hyperfine coupling constants of radical **10** and of the DMF dimer). Radicals **R1** and **R2** were optimised using the UHF method and the 3-21G basis set, frequency analysis was performed on the same level to obtain the zero point energies and then accurate electronic energies were obtained by single point calculations using the DFT method UB3PW91 and the 6-31G* basis set. To calculate the isotropic hyperfine coupling constants of radical **10** the radical **R1** was reoptimised with the UB3PW91 method and the 6-31G* basis set. The coupling constants were obtained by single point calculations with the same method and the 6-311++G** basis set. DMF and its dimer were optimised at B3PW91/6-31G*, frequency analysis was performed on the same level to obtain the zero point energies and then accurate electronic energies were obtained by single point calculations at B3PW91/6-311++G** level.

### Synthesis of *N*-methyl-4-oxo-4-phenylbutananilide 1g

*Anilide* **1g** (3.78 g, 47%) was obtained from *N*-methylaniline (3.26 g, 30.0 mmol) and the mixed anhydride of 4-oxo-4-phenylbutanoic acid **4** (5.35 g, 30.0 mmol), according to literature,[10] as a white solid ($R_f$ = 0.50, $CH_2Cl_2$–MeOH = 100 : 2), mp 69–71 °C (Found: C, 76.14; H, 6.49; N, 5.05. $C_{17}H_{17}NO_2$ requires C, 76.38; H, 6.41; N, 5.24%); $\lambda_{max}$(MeCN)/nm 238 (log ε 4.27), 275 (3.02) and 309 (1.85); $\nu_{max}$(KBr)/cm$^{-1}$ 1682 (CO), 1654 (CO), 1594, 1494 and 699; $\delta_H$(300 MHz; $CDCl_3$) 2.50 (2 H, t, $J$ 6.4, 2-C$H_2$), 3.29 (5 H, m, N-C$H_3$, 3-C$H_2$) and 7.30–7.99 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 28.4 (t), 33.8 (t), 37.3 (q, N-*C*H$_3$), 127.4 (d), 127.8 (d), 128.0 (d), 128.2 (d), 129.8 (d), 132.9 (d), 136.7 (s), 143.9 (s), 171.8 (s, C-1) and 199.0 (s, C-4); *m*/*z* (EI) 267 (M$^+$, 1%), 161 (44), 133 (15), 107 (100), 77 (69) and 51 (28).

### General procedure for the photopinacolisation of amides 1 and acid 4

Irradiations of amides **1** and acid **4** were performed in dry diethyl ether with concentrations of approximately 1 mg cm$^{-3}$. The solutions were degassed with argon for 30 minutes before irradiation with a high pressure mercury arc lamp (150 W). Products **2**, **3** and a mixture of **5** and **6** were separated by fractional crystallisation or by flash chromatography. Pinacols **2** and **3** were identified by HPLC using a chiral stationary phase. Chromatograms of racemic products **3** display two peaks for both enantiomers, while only one peak is observed for *meso*-products **2**.

### (4*RS*,5*SR*)-1,8-Di(azetidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2a and (±)-1,8-di(azetidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3a

4-Azetidin-1-yl-1-phenylbutane-1,4-dione **1a** (396 mg, 1.82 mmol) was irradiated in diethyl ether (230 cm$^3$). **2a** (55 mg, 13%) precipitated after removal of most of the solvent to give a white solid. Crystalline **3a** (132 mg, 31%) was obtained after cooling of the filtrate to −20 °C. Single crystals of **3a**, suitable for X-ray analysis, were obtained from $CH_2Cl_2$–petrol ether. **2a**: mp 213–220 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3432, 3192, 1609 (CO), 1476, 1442, 1055 and 697; $\delta_H$(300 MHz; $CDCl_3$) 1.72–2.15 (10 H, m), 2.50–2.55 (2 H, m), 3.71–3.88 (8 H, m), 5.49 (2 H, s, 2 × OH) and 7.18–7.60 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 14.8 (2 × t), 26.0 (2 × t), 30.0 (2 × t), 47.8 (2 × t, N-*C*H$_2$), 50.0 (2 × t, N-*C*H$_2$), 80.4 (2 × s, C-4, C-5), 126.2 (2 × d), 127.1 (2 × d), 128.4 (2 × d), 143.1 (2 × s) and 174.3 (2 × s, C-1, C-8); *m*/*z* (EI) 436 (M$^+$, 0%), 218 (60), 161 (100), 133 (19), 115 (14), 105 (77), 99 (37), 77 (42) and 58 (90). **3a**: mp 175–178 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3417 (OH), 1637 (CO), 1611 (CO), 1457, 1440 and 706; $\delta_H$(300 MHz; $CDCl_3$) 1.83–1.95 (5 H, m), 2.07–2.18 (5 H, m), 2.35–2.45

(2 H, m), 3.83–3.92 (8 H, m), 5.68 (2 H, s, 2 × OH) and 7.20–7.39 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 14.7 (2 × t), 25.7 (2 × t), 29.9 (2 × t), 47.7 (2 × t, N-*C*$H_2$), 50.0 (2 × t, N-*C*$H_2$), 80.7 (2 × s, C-4, C-5), 126.6 (2 × d), 127.0 (2 × d), 128.5 (2 × d), 140.9 (2 × s) and 174.3 (2 × s, C-1, C-8); *m*/*z* (EI) 436 ($M^+$, 0%), 218 (44), 161 (78), 133 (18), 115 (14), 105 (56), 99 (24), 77 (45) and 58 (100).

### (4*RS*,5*SR*)-1,8-Di(pyrrolidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2b and (±)-1,8-di(pyrrolidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3b

After irradiation of 4-pyrrolidin-1-yl-1-phenylbutane-1,4-dione **1b** (482 mg, 2.09 mmol) in diethyl ether (230 $cm^3$) white crystals of **2b** (62 mg, 13%) were filtered from the suspension. FC ($CH_2Cl_2$–MeOH = 100 : 3) of the residue afforded **3b** (59 mg, 12%) as a white solid. **2b**: mp 264–266 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 3437 (OH), 1615 (CO), 1452 and 704; $\delta_H$(300 MHz; $CDCl_3$) 1.72–1.98 (12 H, m), 2.14–2.21 (2 H, m), 2.53–2.59 (2 H, m), 3.00–3.13 (4 H, m), 3.27–3.32 (4 H, m), 5.72 (2 H, s, 2 × OH) and 7.18–7.61 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 24.2 (2 × t), 25.8 (2 × t), 29.9 (2 × t), 30.2 (2 × t), 45.7 (2 × t, N-*C*$H_2$), 46.6 (2 × t, N-*C*$H_2$), 80.5 (2 × s, C-4, C-5), 126.1 (2 × d), 127.0 (2 × d), 128.5 (2 × d), 143.4 (2 × s) and 173.1 (2 × s, C-1, C-8); *m*/*z* (EI) 464 ($M^+$, 0%), 232 (38), 161 (67), 133 (17), 115 (11), 113 (53), 105 (59), 77 (27), 70 (39), 55 (31) and 43 (32). **3b**: mp 40–42 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 2973, 2875, 1614 (CO), 1448, 758 and 705; $\delta_H$(300 MHz; $CDCl_3$) 1.74–1.83 (8 H, m), 1.96–2.02 (2 H, m), 2.06–2.126 (4 H, m), 2.48–2.57 (2 H, m), 3.12–3.17 (4 H, m), 3.33–3.39 (4 H, m), 5.81 (2 H, s, 2 × OH) and 7.19–7.31 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 24.2 (2 × t), 25.8 (2 × t), 29.5 (2 × t), 30.0 (2 × t), 45.7 (2 × t, N-*C*$H_2$), 46.7 (2 × t, N-*C*$H_2$), 80.7 (2 × s, C-4, C-5), 126.5 (2 × d), 126.9 (2 × d), 128.4 (2 × d), 141.3 (2 × s) and 173.0 (2 × s, C-1, C-8); *m*/*z* (EI) 464 ($M^+$, 0%), 232 (14), 161 (43), 149 (55), 127 (15), 113 (17), 105 (28), 98 (12), 83 (100), 77 (18), 72 (69), 70 (19), 55 (45), 47 (78) and 43 (69).

### (4*RS*,5*SR*)-1,8-Di(piperidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2c and (±)-1,8-di(piperidin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3c

**2c** (64 mg, 12%) was obtained as a white solid after filtration *via* photoreduction of 4-piperidin-1-yl-1-phenylbutane-1,4-dione **1c** (520 mg, 2.12 mmol) in diethyl ether (230 $cm^3$), followed by removal of most of the solvent. **3c** (180 mg, 34%) was isolated as a white solid by FC ($CH_2Cl_2$–MeOH = 100 : 3) of the residue. **2c**: mp 237–238 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 3317, 3241, 1613 (CO), 1447, 1250 and 1229; $\delta_H$(300 MHz; $CDCl_3$) 1.25–1.52 (12 H, m), 1.88–2.03 (4 H, m), 2.17–2.24 (2 H, m), 2.50–2.58 (2 H, m), 3.08–3.15 (4 H, m), 3.33–3.47 (4 H, m), 5.44 (2 H, s, 2 × OH) and 7.18–7.55 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 24.3 (2 × t), 25.4 (2 × t), 26.0 (2 × t), 28.3 (2 × t), 30.3 (2 × t), 42.9 (2 × t, N-*C*$H_2$), 46.6 (2 × t, N-*C*$H_2$), 80.5 (2 × s, C-4, C-5), 126.2 (2 × d), 127.1 (2 × d), 128.3 (2 × d), 143.1 (2 × s) and 172.7 (2 × s, C-1, C-8); *m*/*z* (EI) 492 ($M^+$, 0%), 246 (37), 161 (70), 133 (13), 127 (48), 105 (44), 86 (100), 84 (26) and 77 (17). **3c**: mp 29–33 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 3422 (OH), 2936, 1615 (CO), 1444 and 705; $\delta_H$(300 MHz; $CDCl_3$) 1.10–1.24 (1 H, m), 1.342–1.52 (12 H, m), 1.85–1.87 (1 H, m), 2.07–2.16 (4 H, m), 2.42–2.51 (2 H, m), 3.13–3.19 (4 H, m), 3.38–3.45 (4 H, m), 5.63 (2 H, s, 2 × OH) and 7.13–7.22 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 24.3 (2 × t), 25.4 (2 × t), 26.1 (2 × t), 27.9 (2 × t), 30.3 (2 × t), 42.9 (2 × t, N-*C*$H_2$), 46.7 (2 × t, N-*C*$H_2$), 80.8 (2 × s, C-4, C-5), 126.5 (2 × d), 127.0 (2 × d), 128.4 (2 × d), 141.2 (2 × s) and 172.7 (2 × s, C-1, C-8); *m*/*z* (EI) 492 ($M^+$, 0%), 246 (32), 161 (92), 133 (14), 127 (16), 105 (36), 86 (100), 84 (26) and 77 (18).

### (4*RS*,5*SR*)-1,8-Di(azepanin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2d and (±)-1,8-di(azepanin-1-yl)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3d

4-Azepanin-1-yl-1-phenylbutane-1,4-dione **1d** (486 mg, 1.87 mmol) was irradiated in diethyl ether (500 $cm^3$). **2d** (55 mg, 11%) was filtered as a white solid. Gel chromatography (Sephadex LH-20, $CH_2Cl_2$–MeOH = 3 : 1) of the filtrate yielded **3d** (19 mg, 4%) as a white solid. **2d**: mp 173–183 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 3219 (OH), 2925, 1611 (CO), 1598, 1440 and 704; $\delta_H$(300 MHz; $CDCl_3$) 1.31–1.61 (16 H, m), 1.84–2.05 (4 H, m), 2.15–2.24 (2 H, m), 2.49–2.57 (2 H, m), 3.06–3.17 (4 H, m), 3.26–3.51 (4 H, m), 5.54 (2 H, s, 2 × OH) and 7.17–7.60 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 26.6 (2 × t), 27.2 (4 × t), 28.3 (2 × t), 28.5 (2 × t), 30.2 (2 × t), 46.2 (2 × t, N-*C*$H_2$), 47.9 (2 × t, N-*C*$H_2$), 80.5 (2 × s, C-4, C-5), 126.1 (2 × d), 127.0 (2 × d), 128.4 (2 × d), 143.3 (2 × s) and 174.1 (2 × s, C-1, C-8); *m*/*z* (EI) 520 ($M^+$, 0%), 260 (53), 161 (100), 154 (12), 141 (38), 133 (23), 126 (23), 115 (14), 105 (68), 100 (81), 98 (28) and 77 (28). **3d**: mp 105–115 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 3424 (OH), 2927, 1614 (CO), 1445 and 705; $\delta_H$(300 MHz; $CDCl_3$) 1.44–1.64 (16 H, m), 2.00–2.18 (6 H, m), 2.53–2.58 (2 H, m), 3.19–3.45 (8 H, m), 5.71 (2 H, s, 2 × OH) and 7.16–7.35 (m, 10 H, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 26.6 (2 × t), 26.8 (2 × t), 27.3 (2 × t), 28.1 (2 × t), 28.6 (2 × t), 30.2 (2 × t), 46.2 (2 × t, N-*C*$H_2$), 47.9 (2 × t, N-*C*$H_2$), 80.9 (2 × s, C-4, C-5), 126.4 (2 × d), 126.9 (2 × d), 128.4 (2 × d), 141.5 (2 × s) and 174.2 (2 × s, C-1, C-8); *m*/*z* (EI) 520 ($M^+$, 0%), 260 (43), 182 (13), 161 (100), 154 (23), 141 (25), 133 (27), 126 (17), 115 (15), 105 (68), 100 (76), 98 (53) and 77 (46).

### (4*RS*,5*SR*)-1,8-Di(morpholino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2e and (±)-1,8-di(morpholino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3e

The photoreduction of 1-morpholino-4-phenylbutane-1,4-dione **1e** (458 mg, 1.85 mmol) was carried out in diethyl ether (230 $cm^3$). Dimorpholide **2e** (36 mg, 7%) was isolated as a white solid by filtration from the reaction mixture. FC ($CH_2Cl_2$–MeOH = 100 : 3) of the residue afforded dimorpholide **3e** (110 mg, 23%) as a white solid. **2e**: mp 205–220 °C (lit.,[10] 235–237 °C); $\nu_{max}$(KBr)/$cm^{-1}$ 3437 (OH), 1616 (CO), 1444, 1237, 1114 and 707; $\delta_H$(300 MHz; $CDCl_3$) 1.90–2.25 (6 H, m), 2.52–2.59 (2 H, m), 3.10–3.27 (4 H, m), 3.40–3.65 (12 H, m), 5.08 (2 H, s, 2 × OH) and 7.22–7.60 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 28.0 (2 × t), 30.2 (2 × t), 42.1 (2 × t, N-*C*$H_2$), 45.8 (2 × t, N-*C*$H_2$), 66.2 (2 × t, O-*C*$H_2$), 66.6 (2 × t, O-*C*$H_2$), 80.5 (2 × s, C-4, C-5), 126.5 (2 × d), 127.3 (2 × d), 128.2 (2 × d), 142.6 (2 × s) and 173.2 (2 × s, C-1, C-8); *m*/*z* (EI) 496 ($M^+$, 0%), 248 (26), 161 (100), 133 (17), 129 (27), 105 (47), 88 (30), 77 (18) and 55 (16); *m*/*z* (FAB, 3-nitrobenzyl alcohol) 497 ($M^+ + 1$); *m*/*z* (CI, isobutane) 497 ($M^+ + 1$). **3e**: mp 68–70 °C (lit.,[10] 168–169 °C); $\nu_{max}$(KBr)/$cm^{-1}$ 3437 (OH), 1639 (CO), 1619 (CO), 1444, 1270, 1115 and 707; $\delta_H$(300 MHz; $CDCl_3$) 1.88–1.97 (2 H, m), 2.10–2.14 (4 H, m), 2.46–2.56 (2 H, m), 3.22–3.25 (4 H, m), 3.45–3.61 (12 H, m), 5.42 (2 H, s, 2 × OH) and 7.23–7.27 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 27.6 (2 × t), 30.1 (2 × t), 44.0 (2 × t, N-*C*$H_2$), 45.9 (2 × t, N-*C*$H_2$), 66.3 (2 × t, O-*C*$H_2$), 66.7 (2 × t, O-*C*$H_2$), 80.8 (2 × s, C-4, C-5), 126.8 (2 × d), 127.1 (2 × d), 128.4 (2 × d), 140.7 (2 × s) and 173.2 (2 × s, C-1, C-8); *m*/*z* (EI) 496 ($M^+$, 0%), 248 (28), 161 (100), 133 (14), 129 (23), 105 (41), 88 (27), 77 (15) and 55 (11); *m*/*z* (FAB, 3-nitrobenzyl alcohol) 497 ($M^+ + 1$).

### (4*RS*,5*SR*)-1,8-Di(*N*,*N*-dimethylamino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2f and (±)-1,8-di(*N*,*N*-dimethylamino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3f

*N*,*N*-Dimethyl-4-oxo-4-phenylbutanamide **1f** (555 mg, 2.71 mmol) was irradiated in diethyl ether (230 $cm^3$). Compound **2f** precipitated after removal of most of the solvent, diamide **2f** (77 mg, 14%) was filtered off. Crystalline diamide **3f** (85 mg,

15%) was obtained after cooling of the filtrate to −20 °C. **2f**: mp 240–241 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3223 (OH), 1616 (CO), 1400, 1160 and 702; $\delta_H$(300 MHz; $CDCl_3$) 1.83–2.58 (8 H, m, 2 × C$H_2$-C$H_2$), 2.73 (6 H, s, 2 × N-C$H_3$), 2.80 (6 H, s, 2 × N-C$H_3$), 5.47 (2 H, s, 2 × OH) and 7.20–7.56 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 28.5 (2 × t), 30.2 (2 × t), 35.6 (2 × q, N-*C*H$_3$), 37.3 (2 × q, N-*C*H$_3$), 80.5 (2 × s, C-4, C-5), 126.2 (2 × d), 127.1 (2 × d), 128.3 (2 × d), 143.1 (2 × s) and 174.7 (2 × s, C-1, C-8); *m*/*z* (EI) 412 ($M^+$, 0%), 206 (48), 161 (100), 133 (16), 105 (51), 87 (52), 77 (20), 72 (15) and 46 (74). **3f**: mp 136–138 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3406 (OH), 1620 (CO), 1154 and 704; $\delta_H$(300 MHz; $CDCl_3$) 1.91–2.56 (8 H, m, 2-C$H_2$-C$H_2$), 2.79 (6 H, s, 2 × N-C$H_3$), 2.85 (6 H, s, 2 × N-C$H_3$), 5.65 (2 H, s, 2 × OH) and 7.20–7.41 (10 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 28.1 (2 × t), 30.0 (2 × t), 35.6 (2 × q, N-*C*H$_3$), 37.3 (2 × q, N-*C*H$_3$), 80.8 (2 × s, C-4, C-5), 126.5 (2 × d), 127.0 (2 × d), 128.4 (2 × d), 141.1 (2 × s) and 174.6 (2 × s, C-1, C-8); *m*/*z* (EI) 412 ($M^+$, 0%), 206 (42), 161 (100), 133 (16), 105 (53), 87 (43), 77 (23), 72 (16) and 46 (77).

### (4*RS*,5*SR*)-1,8-Di(*N*-methylanilino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2g and (±)-1,8-di(*N*-methylanilino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3g

Irradiation of 1-(*N*-methylanilino)-4-phenylbutane-1,4-dione **1g** (505 mg, 1.89 mmol) in diethyl ether (230 cm$^3$) yielded white precipitate **2g** after removal of most of the solvent, diamide **2g** (57 mg, 11%) was filtered off. Cooling of the filtrate to −20 °C afforded diamide **3g** (116 mg, 23%) as a white solid. **2g**: mp 132–135 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3463 (OH), 1647 (CO), 1618 (CO), 1593, 1494 and 703; $\delta_H$(300 MHz; $CDCl_3$) 1.73–1.88 (6 H, m), 2.34–2.41 (2 H, m), 3.16 (6 H, s, 2 × N-C$H_3$), 5.44 (2 H, s, 2 × OH) and 6.89–7.26 (20 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 29.0 (2 × t), 30.6 (2 × t), 37.5 (2 × q, N-*C*H$_3$), 80.7 (2 × s, C-4, C-5), 126.2 (d), 126.4 (d), 126.8 (d), 126.9 (d), 127.6 (d), 128.3 (d), 129.6 (d), 140.8 (2 × s), 143.6 (2 × s) and 174.9 (2 × s, C-1, C-8); *m*/*z* (EI) 536 ($M^+$, 0%), 268 (13), 161 (100), 149 (12), 133 (15), 105 (45) and 77 (32). **3g**: mp 224–226 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3414 (OH), 1637 (CO), 1594, 1495 and 700; $\delta_H$(300 MHz; $CDCl_3$) 1.69–1.93 (6 H, m), 2.37–2.43 (2 H, m), 3.16 (6 H, s, 2 × N-C$H_3$), 5.17 (2 H, s, 2 × OH) and 6.81–7.43 (20 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 29.4 (2 × t), 30.7 (2 × t), 37.5 (2 × q, N-*C*H$_3$), 80.3 (2 × s, C-4, C-5), 126.1 (d), 126.9 (d), 127.0 (d), 127.7 (d), 128.3 (d), 129.6 (d), 142.9 (2 × s), 143.5 (2 × s) and 174.9 (2 × s, C-1, C-8); *m*/*z* (EI) 536 ($M^+$, 0%), 268 (15), 161 (100), 149 (12), 133 (14), 105 (45) and 77 (35); *m*/*z* (CI, isobutane) 537 ($M^+ + 1$).

### (4*RS*,5*SR*)-1,8-Di(*N*-benzyl-*N*-methylamino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2h and (±)-1,8-di(*N*-benzyl-*N*-methylamino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3h

*N*-Benzyl-*N*-methyl-4-oxo-4-phenylbutanamide **1h** (528 mg, 1.88 mmol) was irradiated in diethyl ether (230 cm$^3$). After removal of most of the solvent, diamide **2h** was isolated by filtration as a white solid (43 mg, 8%). Cooling of the filtrate to −20 °C gave diamide **3h** (67 mg, 13%) as a white solid, which was filtered. **2h**: mp 149–151 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3223 (OH), 1625 (CO) and 703; $\delta_H$(300 MHz; $CDCl_3$) 1.87–2.64 (8 H, m, 2 × C$H_2$-C$H_2$), 2.62 (6 H, s, 2 × N-C$H_3$), 4.23–4.45 (4 H, m, 2 × Ph-C$H_2$), 5.38 (2 H, s, 2 × OH) and 6.85–7.70 (20 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 28.5 (t), 28.8 (t), 30.2 (2 × t), 34.0 (q, N-*C*H$_3$), 34.8 (q, N-*C*H$_3$), 51.0 (t, Ph-*C*H$_2$), 53.3 (t, Ph-*C*H$_2$), 80.6 (2 × s, C-4, C-5), 126.2 (d), 126.3 (d), 127.2 (d), 127.3 (d), 127.5 (d), 128.3 (d), 128.5 (d), 128.8 (d), 135.9 (s), 136.9 (s), 143.0 (2 × s) and 174.8 (2 × s, C-1, C-8); *m*/*z* (EI) 565 ($M^+$, 0.2%), 282 (24), 163 (19), 161 (52), 122 (30), 120 (34), 105 (30), 91 (100), 77 (16) and 42 (11). **3h**: mp 190–192 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3437 (OH), 1629 (CO) and 705; $\delta_H$(300 MHz; $CDCl_3$) 1.94–2.63 (8 H, m, 2 × C$H_2$-C$H_2$), 2.68 (3 H, s, N-C$H_3$), 2.83 (3 H, s, N-C$H_3$), 4.28–4.50 (4 H, m, 2 × Ph-C$H_2$), 5.50–5.64 (2 H, m, 2 × OH) and 6.90–7.31 (20 H, m, arom. H); $\delta_C$(75.5 MHz; $CDCl_3$) 28.1 (t), 28.4 (t), 30.1 (t), 30.3 (t), 34.0 (q, N-*C*H$_3$), 34.9 (q, N-*C*H$_3$), 51.0 (t, Ph-*C*H$_2$), 53.3 (t, Ph-*C*H$_2$), 80.9 (2 × s, C-4, C-5), 126.2 (d), 126.6 (d), 127.0 (d), 127.3 (d), 127.4 (d), 127.9 (d), 128.4 (d), 128.5 (d), 128.8 (d), 136.6 (s), 137.0 (s), 141.0 (2 × s), 174.7 (s) and 175.0 (s); *m*/*z* (EI) 565 ($M^+$, 0.2%), 282 (36), 163 (21), 161 (61), 122 (30), 120 (34), 105 (30), 91 (100), 77 (16) and 42 (10).

### (4*RS*,5*SR*)-1,8-Di(*N*-benzylamino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 2i and (±)-1,8-di(*N*-benzylamino)-4,5-dihydroxy-4,5-diphenyloctane-1,8-dione 3i

Photoreduction of *N*-benzyl-4-oxo-4-phenylbutanamide **1i** (511 mg, 1.29 mmol) in diethyl ether (500 cm$^3$) afforded after FC ($CH_2Cl_2$–MeOH = 100 : 1.5) diamides **2i** (51 mg, 15%) and **3i** (34 mg, 10%). **2i**: mp 188–190 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3319 (OH), 1627 (CO), 1552 and 702; $\delta_H$(300 MHz; DMSO) 1.46–1.91 (6 H, m), 2.25–2.27 (1 H, m), 2.71–2.72 (1 H, m), 4.09–4.12 (4 H, m, 2 × Ph-C$H_2$), 5.24 (2 H, s, 2 × OH), 7.08–7.46 (20 H, m, arom. H) and 8.12–8.19 (2 H, m, 2 × NH); $\delta_C$(75.5 MHz; DMSO) 30.2 (2 × t), 31.1 (2 × t), 42.0 (2 × t, Ph-*C*H$_2$), 80.0 (2 × s, C-4, C-5), 126.0 (d), 126.7 (d), 126.8 (d), 127.0 (d), 128.2 (d), 139.5 (2 × s), 143.4 (2 × s) and 173.2 (2 × s, C-1, C-8); *m*/*z* (EI) 536 ($M^+$, 0%), 268 (11), 251 (20), 161 (55), 115 (11), 106 (34), 105 (34), 91 (100) and 77 (25). **3i**: mp 168–170 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 2926, 1627 (CO), 1452 and 702; $\delta_H$(300 MHz; DMSO) 1.65–1.73 (6 H, m), 2.00–2.34 (2 H, m), 4.09–4.24 (4 H, m, 2 × Ph-C$H_2$), 5.21 (2 H, s, 2 × OH), 7.04–7.47 (20 H, m, arom. H) and 8.15–8.22 (2 H, m, 2 × NH); $\delta_C$(75.5 MHz; DMSO) 30.5 (4 × t), 42.2 (2 × t, Ph-*C*H$_2$), 80.5 (2 × s, C-4, C-5), 126.0 (d), 126.5 (d), 126.8 (d), 127.3 (d), 128.0 (d), 128.3 (d), 139.7 (2 × s), 142.4 (2 × s) and 173.3 (2 × s, C-1, C-8); *m*/*z* (EI) 536 ($M^+$, 0%), 268 (21), 162 (12), 161 (19), 133 (14), 106 (72), 91 (100), 77 (48) and 65 (16).

### (±)-2,2′-Diphenyltetrahydro[2,2′]bifuranyl-5,5′-dione 5 and (2*RS*,2′*SR*)-2,2′-diphenyltetrahydro[2,2′]bifuranyl-5,5′-dione 6

4-Oxo-4-phenylbutanoic acid **4** (345 mg, 1.94 mmol) was irradiated in diethyl ether (100 cm$^3$). A 1 : 1 mixture of **5** and **6** (71 mg, 24%) determined by NMR spectroscopy was obtained from diethyl ether–petrol ether. Product **6** was obtained as crystals, suitable for X-ray analysis from $CH_2Cl_2$; mp 264–267 °C (lit.,[12] >250 °C).

### Crystal structure determination of compounds 3a and 6‡

**Crystal data for 3a.** $C_{26}H_{32}N_2O_4$, $M = 436.552$, monoclinic, $a = 10.118(1)$, $b = 10.114(2)$, $c = 11.853(1)$ Å, $\alpha = 90$, $\beta = 104.172(6)$, $\gamma = 90°$, $U = 1176.0(2)$ Å$^3$, $T = 298$ K, space group $P2_1$ (no. 4), $Z = 2$, $\mu$(Cu-K$_\alpha$) = 0.63 mm$^{-1}$, 2663 reflections measured, 2535 unique ($R_{int} = 0.05$) which were used in all calculations. The final $wR(F^2)$ was 0.040 (all data).

**Crystal data for 6.** $C_{20}H_{18}O_4$, $M = 322.360$, monoclinic, $a = 9.497(1)$, $b = 8.421(1)$, $c = 10.087(1)$ Å, $\alpha = 90$, $\beta = 95.91(1)$, $\gamma = 90°$, $U = 802.4(25)$ Å$^3$, $T = 293(2)$ K, space group $P2_1/c$ (no. 14), $Z = 2$, $\mu$(Mo-K$_\alpha$) = 0.093 mm$^{-1}$, 3130 reflections measured, 1401 unique ($R_{int} = 0.0214$) which were used in all calculations. The final $wR(F^2)$ was 0.0818 (all data).

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‡ CCDC reference number 188/178. See http://www.rsc.org/suppdata/p2/1999/2029 for crystallographic files in .cif format.

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