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Photoinitiated Domino Reactions: *N*-(Adamantyl)phthalimides and *N*-(Adamantylalkyl)phthalimides

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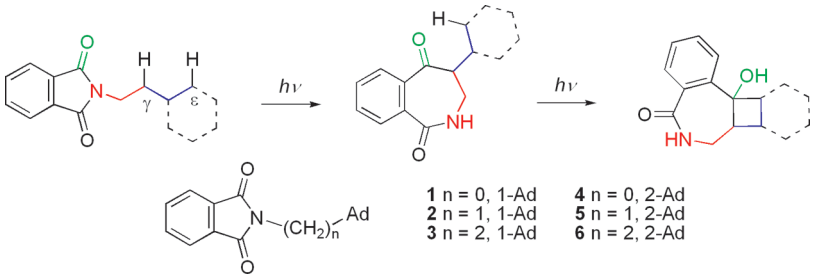

Phthalimides **1**−**6** undergo photochemical reactions upon direct irradiation as well as triplet sensitization and give rise to new products. Besides formation of the primary photoproducts, the first photochemical step initiates a subsequent thermal domino reaction or a domino sequence of a thermal and a photochemical reaction. The latter, involving two photochemical intramolecular γ-H abstractions, was observed with phthalimides **1**, **3**, and **6** and delivered stereospecifically the hexacyclic benzazepine products **12**, **19**, and **27**, respectively. The lowest triplet states of **1**−**6** were characterized in several solvents upon direct and acetone-sensitized excitation. The intermolecular electron transfer from triethylamine and DABCO was studied, and the radical anions were observed. Electrochemical measurements showed that intramolecular electron transfer from the adamantyl group of **1**−**6** to the lowest triplet state of the phthalimides is not feasible. The formation of products can be explained by intramolecular H-abstraction from the (alkyl)adamantane to the excited phthalimide, either from the excited singlet state or a hidden upper excited triplet state.

Introduction

A major challenge in modern chemical technology is the search for environment-friendly procedures, with a maximum preservation of resources and minimal production of waste. Consequently, today it is not a question of what we can synthesize, but rather how we can do it economically. A logical solution to these increasing demands is the use of the modern synthetic methods based on multicomponent[1] or domino reactions.[2] Domino reactions initiated by photons appear to be particularly interesting in the context of green chemistry since photons are the most eco-friendly, practically traceless reagents. One representative elegant example for the use of a photochemical domino reaction in synthesis is the formation of enantiomerically pure estrone wherein photochemically generated *o*-quinodimethane reacts in an intramolecular Diels−Alder reaction.[3] Another example, synthesis of grayanotoxin, is accomplished by use of a photochemical meta cycloaddition in a domino sequence.[4] Examples involving photochemical steps, followed by a Diels−Alder domino reaction

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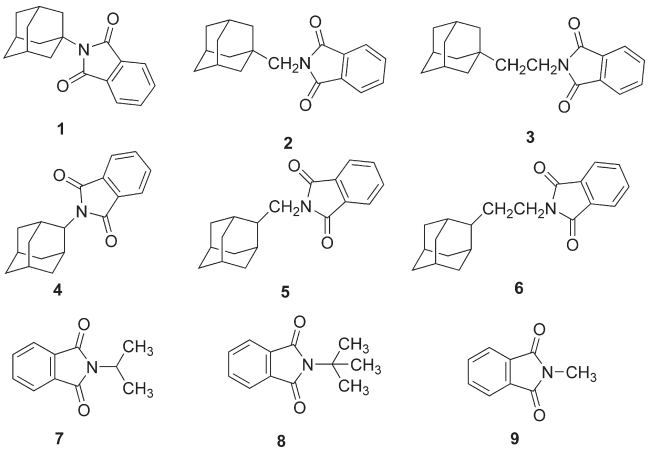
are also synthesis of hexacyclic products from bishomosecoheptaprismane,[5] or synthesis of dihydropentalenes.[6] Further examples involve photoinitiated oxidative electron transfer giving rise to radical cations, which undergo domino reaction sequences.[7] Photoinitiated domino reactions have been used in the synthesis of iridoids and secoiridoids[8] or synthesis of dihydropyridines.[9] However, not many more examples of these types are known since photochemical reactions often produce stable photoproducts that do not undergo further thermal reactions, or else the chromophore involved in the first photochemical process is often modified during the reaction and is not available for a second photochemical step.

Recently we reported a novel photoinitiated domino process of *N*-(1-adamantyl)phthalimide (**1**) that gives rise to a highly complex methanoadamantane-benzazepine derivative, involving two consecutive photochemical γ-hydrogen abstractions.[10] Furthermore, we reported on the syntheses of a series of adamantyl phthalimides **1**−**6** and an investigation of their photochemical reactivity in the solid state.[11] Phthalimide is a chromophore from the well-known family of aromatic imides that has received considerable attention in

CHART 1



view of its photophysics[12,13] and application in photochemical synthesis[14−16] and has therefore been reviewed by Griesbeck et al.[17] and others.[18] In the context of our research on functionalizations of various cage molecules (adamantane, noradamantane, protoadamantane, PCU)[19,20] we turned our attention to photochemical transformations of adamantyl phthalimides for the preparation of potentially biologically active molecules. That research was primarily fuelled by the discovery that numerous spiro-fused adamantane derivatives showed pronounced antiviral and anticancer activity.[21]

Here we report on a thorough investigation of the photochemical reactivity of adamantylphthalimides **1**−**6** with the aim of finding suitable substrates and photolysis conditions that will give rise to the domino photochemical processes. The adamantyl derivatives were chosen because of their rigid structure wherein cleavages by Norrish type II reaction are not possible or are unlikely. Besides, we are interested in the preparation of complex adamantyl derivatives for the purpose of studying their biological activity. Phthalimides **1**−**6** were irradiated under various conditions, and their photoproducts

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TABLE 1. Photolysis of Phthalimides 1−6 in Several Solvents under N_2[a]

				product yields (%)[c]		
compound	solvent	time (h)	conversion[b] (%)	I[d]	II[e]	III[f]
1	cyclohexane	16	< 1			**12** (< 1)
	acetone	2	20			**12** (20)
	acetone−H_2O (3:1)	2	60			**12** (60)
	CH_3CN	16	11			**12** (11)
	CH_3CN−H_2O (3:1)	16	18			**12** (18)
2	acetone	15	70	**14** (5−10)		
	acetone−H_2O (3:1)	15	33		**15** (5)	
	CH_3CN	8	17	**13** (3), **14** (8)	**15** (1), **16** (1)	
	CH_3CN	24	54	**13** (5), **14** (2)	**15** (5), **16** (30)	
3	acetone	2	10		**18** (2)	**19** (4)
	CH_3CN	2	16	**17** (2)	**18** (6)	**19** (6)
	CH_3CN−H_2O (3:1)	2	60		**18** (36)	**19** (18)
4	cyclohexane	16	< 3			
	acetone	4	64	**20** (34), **21** (11)	**22** (11)	
	CH_3CN	16	19	**20** (10), **21** (4)	**22** (3)	
5	benzene	16	40			
	acetone	2	23	**24** (< 1)	**23** (13)	
	CH_3CN	2	27	**24** (< 1)	**23** (24)	
	CH_3CN−H_2O (3:1)	2	58	**24** (< 1)	**23** (52)	
6	acetone	2	27	**25** (< 1), **26** (5)		
	CH_3CN	2	37	**25** (4), **26** (17)		**27** (9)
	CH_3CN−H_2O (3:1)	2	43	**25** (4), **26** (11)		**27** (25)

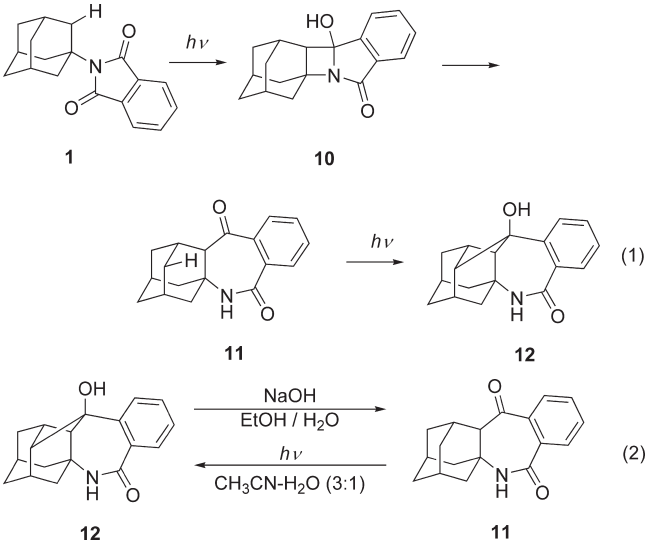
[a]The photolyses were carried out on a semipreparative scale for comparison purpose (some larger scale irradiations presented in the Experimental Section gave higher yields for some products). [b]Obtained from the recovered starting material by column chromatography. [c]Isolated yield. [d]Products of hydrogen abstraction and C−C bond formation. [e]Products of domino reactions involving photochemical and chemical steps. [f]Products of domino reactions involving two photochemical steps and one chemical step.

were isolated and characterized. Furthermore, to get insight into photochemical reactivity, an examination of the photophysics of **1**−**6** by time-resolved methods was carried out and compared to the photophysics of known *N*-alkylphthalimides **7**−**9** (Chart 1). We investigated primarily the conditions that influence the quantum yield of substrate decomposition (Φ_d). Moreover, we were interested as to why photoproducts are formed with a low quantum yield of conversion (Φ_{pr}), whereas in similar photoreactions benzoyl adamantanes give products with a Φ_{pr} that is higher by 2 orders of magnitude.[22] Optimization of the reaction conditions that would increase the quantum yields is especially important in the context of green chemistry. Another question aims at the influence of added water (or protic solvent) on the quantum yield of reactions, which might be due to a switching of the population of the excited triplet states [$^3(n\pi^*)$ or $^3(\pi\pi^*)$]. Finally, we aim at a method of distinguishing the H-transfer mechanism from the mechanism involving coupled electron transfer and proton transfer that was postulated in the previous communication.[10]

Results

Preparative Irradiations. Preparative irradiations were carried out in solvents of different polarity and H-donor ability. Photolyses were not taken to high conversions in order to detect and isolate primary photochemical products. The conversions and the product yields are compiled in Table 1. Generally, photochemical reactivity of phthalimides is very low in cyclohexane or benzene and increases in polar solvents such as CH_3CN. Except for derivative **2**, an addition of H_2O further increases photochemical reactivity. Thus, in CH_3CN−H_2O (3:1), under the same irradiation conditions, conversions were 2−3 times higher than in CH_3CN. The photochemical conversion of phthalimides **1**, **2**, and **4** can be further significantly improved upon irradiation in acetone or acetone−H_2O mixture, as acetone is suggested to act as a triplet sensitizer.

Photochemistry of **1** giving rise to the domino process was reported in our previous communication.[10] Formation of hexacyclic benzazepine product **12** was explained by two consecutive photochemical hydrogen abstractions via azetidinol intermediate **10** and amidoketone **11** (eq 1). To additionally show that two photochemical steps are required to transform phthalimide **1** into **12**, we prepared the keto-azepinone derivative **11** and performed its photolysis. Photolysis of **11** in CH_3CN−H_2O (3:1) gave **12** cleanly and efficiently (eq 2). Compound **11** was obtained from **12** by a careful base-induced cyclobutane ring opening,[23] isolated, and fully characterized by spectroscopic methods.



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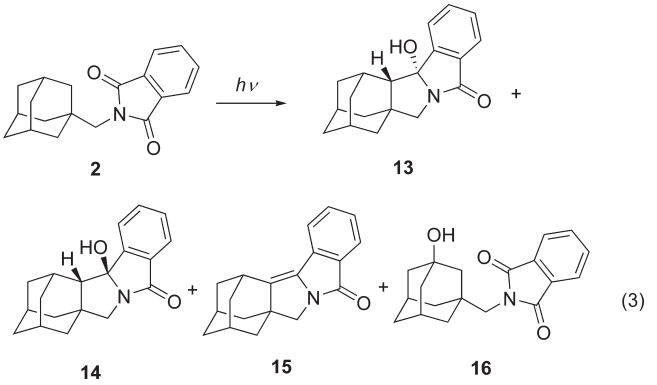
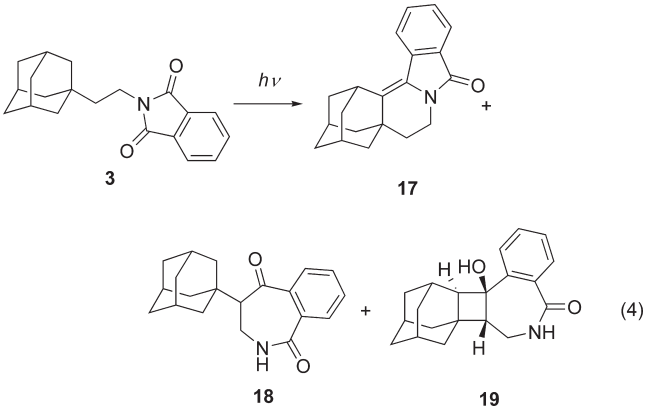
Unlike the photochemical reaction of **1** (eq 1), irradiation of **2** in acetone gave a mixture of many products with acetone, but no attempt was made to characterize these. On the other hand, a low-conversion photolysis of **2** in CH_3CN (eq 3) was reasonably clean and gave rise to three main products, **13**−**15**. Besides products **13**−**15**, alcohol **16** was formed in small amounts, the yield of which increased significantly on prolonged irradiation (Table 1). The structures of **13**−**16** were fully characterized by spectroscopic methods, and in the case of **14** further substantiated by X-ray structural analysis (see Supporting Information).



(3)

The photochemical reaction of **3** gave rise to three products (eq 4). The structures **17**−**19** were determined by spectroscopic methods, and the structure **19** was further proven by X-ray structural analysis (see Supporting Information). In contrast to **2**, the photolysis of **3** was the most efficient in CH_3CN-H_2O (3:1), and the conversion was higher in CH_3CN than in acetone. Further irradiation of the isolated **18** in CH_3CN-H_2O (3:1) cleanly delivers the secondary photoproduct **19**.



(4)

Whereas irradiation of **4** in the solid state gave mainly *endo*-alcohol **21**, photolysis in solution gave a mixture of the three products **20**−**22** (eq 5), wherein *exo*-alcohol **20** predominated.[11] The photochemical reaction of **4** was clearly most efficient in acetone and least in cyclohexane. On addition of H_2O to the CH_3CN solution of **4**, the photochemical reactivity was enhanced. However, almost the same ratio of products was obtained in acetone,

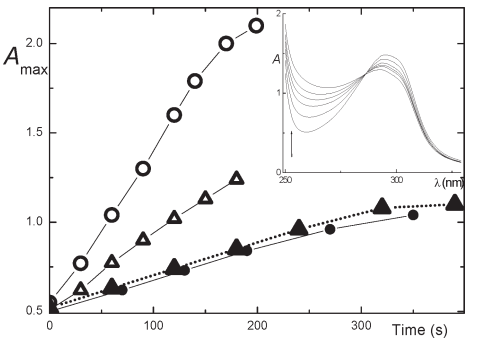
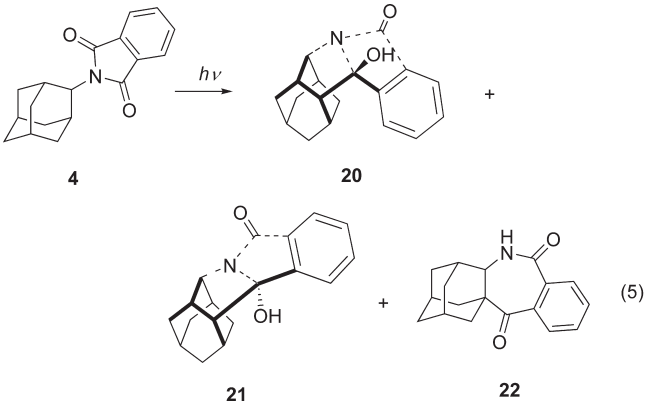


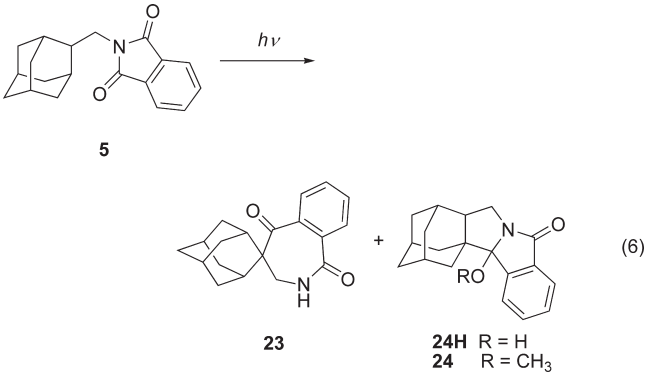
FIGURE 1. Plots of A_{255} for **5** in argon-saturated CH_3CN (Δ), oxygen-saturated CH_3CN (▲), argon-saturated CH_3CN-H_2O (3:1) (○), and oxygen-saturated CH_3CN-H_2O (3:1) (●) as a function of the time of irradiation at 313 nm. Inset: spectra of **5** in argon-saturated CH_3CN, 30 s intervals.

CH_3CN, and CH_3CN-H_2O (3:1).



(5)

Irradiation of **5** in all of the investigated solvents gave rise to one major product, the spiro compound **23**. The photochemical reaction was very clean; besides spiro **23** only traces of **24H** were detected (eq 6). Upon attempts to purify **24H** on a chromatographic column with $CH_2Cl_2-CH_3OH$, **24H** was transformed to the methoxy derivative **24**, which was isolated and fully characterized by spectroscopic methods. The structure of spiro product **23** was proven by X-ray structural analysis (see Supporting Information). The photolysis of **5** was more efficient in CH_3CN than in acetone, and addition of H_2O to the CH_3CN solution further increased the yield of the product **23**. Interestingly, the formation of **23** was found to be only partly quenched by O_2.



(6)

The photolysis of phthalimide **6** furnished three products, **25**−**27** (eq 7), which were isolated and characterized by

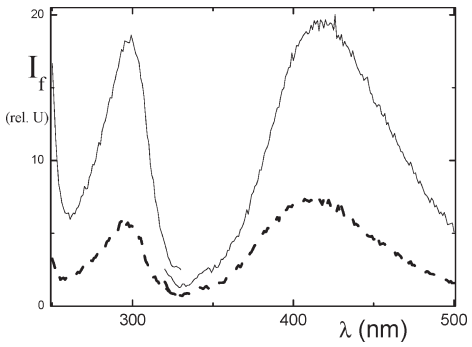
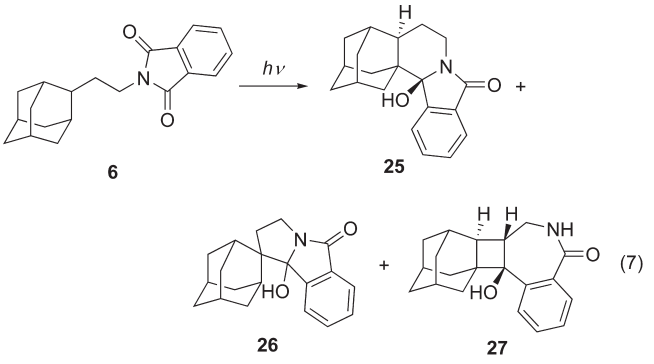


FIGURE 2. Fluorescence excitation (left, λ_f=440 nm) and emission (right, λ_{ex} = 300 nm) spectra of **5** in CH_3CN (broken) and CH_3CN-H_2O (3:1) (unbroken).

spectroscopic methods. The structure of **27** was proven by X-ray structural analysis (see Supporting Information). Analogous to the previous example, the photolysis was more efficient in CH_3CN than in acetone and most efficient in CH_3CN-H_2O (3:1).



(7)

Summarizing the product studies, three families of photoproducts were isolated and characterized for **1**−**6**: (I) primary products which result from the initial H-abstraction and subsequent C−C bond formation, (II) products that result from a domino thermal reaction that follows the initial photochemical step, and (III) products resulting from a second photochemical reaction following (I) and (II).

Quantum Yield of Photoreactions. The quantum yields for the substrate decomposition (Φ_d) were determined by absorption measurements. The absorption spectrum of **5** in argon-saturated CH_3CN has a maximum at 290 nm and a minimum at 255 nm. The latter increases strongly upon continuous irradiation at 313 nm, and the former decreases slightly, thereby showing an isosbestic point at 273 nm (Figure 1, inset). Plots of A_{255} versus time are shown in Figure 1 for several cases. The photoproducts of **1** or **4** in argon-saturated CH_3CN and CH_3CN-H_2O (3:1) are formed with low Φ_d. Alternatively, Φ_{pr}^{rel} of conversion to products was used. Φ_d is largest for **5** in CH_3CN-H_2O (3:1) (Table 2), although Φ_{pr} of **23** is only 0.008, as determined by valerophenone actinometry.

Quenching Measurements. Quenching studies were conducted for the photoreaction of **5** because of its highest quantum yield Φ_{pr} in the series **1**−**6**. The semipreparative photolysis results for **5** in oxygen-saturated CH_3CN-H_2O (3:1) reveal that photoconversion, Φ_{pr} is ca. 20−50% lower than under argon. Similarly, only a small variation in Φ_{pr} due to oxygen versus argon saturation was found for **2** in CH_3CN or CH_3CN-H_2O (3:1). In addition, we attempted to perform the quenching for the photoreaction of **5** by 1,3-pentadiene, the ubiquitous quencher of the triplet excited state of ketones. However, lower concentrations of the quencher (< 0.01 M) did not influence the conversion to the photoproducts, whereas higher concentrations led to a photocycloaddition with the quencher, which complicated the study. In addition, for **2** and **5** in argon-saturated CH_3CN-H_2O (3:1) we found that DABCO (< 10 mM) does not change conversion to the photoproducts. Although electron transfer occurs (vide infra), a subsequent reaction is back electron transfer. Thus DABCO acts as a physical quencher of the lowest triplet state. Quenching by H-atom transfer from 2-propanol to triplet phthalimide is also indicated since a significant decomposition was found for **2**, **3**, **5**, or **6** in argon-saturated CH_3CN within a few minutes of irradiation at 313 nm.

Successful quenching of the photochemical reaction of **5** was performed with biacetyl (E_T = 236 kJ mol^{-1}).[24] Experiments were carried out in CH_3CN-H_2O (3:1) in the concentration range 0.01−0.1 M. Further increase of the quencher concentration (> 0.1 M) did not result in additional quenching; only ~70% of the reaction was quenched. This finding suggests that ~30% of the reaction does not proceed via the involved triplet state. However, in the quenching experiments, the use of 300 nm irradiation also resulted in the excitation of the quencher. Despite this, in the concentration range 0.01−0.03 M a linear Stern−Volmer relationship was obtained, allowing for an estimation of the upper limit of the reactive triplet excited-state lifetime (assuming diffusion-limited quenching characterized by $k_q \sim 1 \times 10^{10}$ M^{-1} s^{-1})[25] in the range ~17 ns, which is surprisingly short in comparison to the measured τ_T (Table 5).

Sensitized Irradiation. Product studies were also carried out for **1** and **5** in the presence of acetophenone and benzophenone. To ensure that only sensitizers absorb, the photolyses were performed at 350 nm in CH_3CN-H_2O (3:1) using 0.1 equiv of the sensitizer. The same products, **12** and **23**, respectively, were found as with direct irradiation, in accordance with the anticipated involvement of the triplet excited state. Furthermore, for phthalimide **5**, a similar efficiency for the sensitization was achieved with benzophenone (E_T = 287 kJ mol^{-1})[24] and acetophenone (E_T = 310 kJ mol^{-1}),[24] suggesting that the energy level of the reactive triplet excited state of **5** is lower than that of benzophenone. On the other hand, in previous a report Wintgens et al.[12g] have shown that the phosphorescence band for **9** is centered at 450 nm and has a lifetime of 1 s at 77 K. That corresponds to the energy level of the $^3(\pi,\pi^*)$ state of **9** E_T = 300 kJ mol^{-1}.[12g] Nevertheless, the simplest sensitization for synthetic purposes (except for **2**) is achieved by irradiating phthalimides in acetone (E_T = 332 kJ mol^{-1}).[24] After removal of the solvent, the mixture of the photoproducts is not contaminated by the sensitizer, which makes isolation easier.

Fluorescence. The fluorescence of **1**−**8** is very weak and similar to that of *N*-alkylphthalimides.[12,13] The fluorescence emission maximum of **5** in CH_3CN-H_2O (3:1) is centered at

(24) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; CRC Taylor and Francis: Boca Raton, 2006.

(25) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834–839.

TABLE 2. Φ_d **Values from Irradiation of Phthalimides 1−6 in Several Solvents**[a]

	Φ_d ($\times 10^{-3}$)			
compound	cyclohexane	CH_3CN	CH_3CN-H_2O (3:1)	TFE[c]
1	0.1	< 0.1	0.1	0.1
2	1.6	1.4	2.4 (0.2)[b]	2.4
3		3.6	6.4	
4	0.3	0.2	0.3	0.3
5	4.0	3.6 (2)	8.0 (3.6)	4.0
6		0.8	3.6	

[a]In argon-saturated solution, λ_{irr} = 313 nm. [b]In parentheses: air-saturated. [c]TFE = trifluoroethanol.

TABLE 3. Φ_f **Values of Phthalimides 1−8 in Polar Solvents**[a]

	Φ_f ($\times 10^{-3}$)	
compound	CH_3CN	CH_3CN-H_2O (3:1)
1	< 0.04	0.05
2	1.4	2.4
3	1.9	5.0
4	< 0.04	0.09
5	1.2	2.4
6	1.1	2.2
7	< 0.04	0.05
8	0.08	0.2

[a]In air-saturated solution, λ_{exc} = 300 nm.

425 nm, and the excitation spectrum (Figure 2) resembles that of absorption spectrum. Similar spectra were recorded for **2**, **3**, and **6** in CH_3CN and mixtures with H_2O. The presence of H_2O slightly red-shifts both spectra. The quantum yield of fluorescence was measured, and the values are compiled in Table 3. Φ_f ranges from < 0.0001 for **1** in CH_3CN to 0.002 for **3** and to 0.005 for **3** in CH_3CN-H_2O (3:1). An enhancement of Φ_f on addition of H_2O to CH_3CN has been reported for other *N*-alkylphthalimides.[12,13]

Triplet Formation and Decay. Pulsed UV excitation of **2**−**6** in solution reveals the lowest triplet state ($^{3*}P$) with maximum at 360 nm and a weak band up to 500 nm. A transient absorption of the biradical intermediates can be excluded. The work of Scaiano, Miranda, and their groups indicate that long-lived biradicals require certain structures that are different from those under examination.[26] Examples of the T-T absorption spectra are shown for **2** and **5** in cyclohexane (Figure 3), for **2** in CH_3CN (Figure 4a) and for **5** in CH_3CN-H_2O (3:1) (Figure 4b). ΔA_{360} at the pulse end (and after a fluorescence peak) as measure of the yield Φ_{isc} was found to be low for **1** and **4** in various solvents and much larger for **2**, **3**, **5** and **6**. The Φ_{isc} values are compiled in Table 4. The observation of $^{3*}P$ for **5** in CH_3CN-H_2O (3:1) is partly overlapped by the fluorescence (Figure 4b, inset), in contrast to cyclohexane, where Φ_f is much lower. A marked change was also found for Φ_{isc} of **7** versus **8**.

The triplet lifetime ($\tau_T = 1/k_{obs}$) under argon and low laser intensity is typically τ_T = 5−10 μs, whereas T-T annihilation contributes to the decay at higher intensities. The results of τ_T are compiled in Table 5. Examples of the kinetics are shown for **1**, **2**, and **5** in cyclohexane, **2** in CH_3CN, and **5** in CH_3CN-H_2O (3:1) (insets of Figures 3 and 4). Oxygen quenches the triplet,

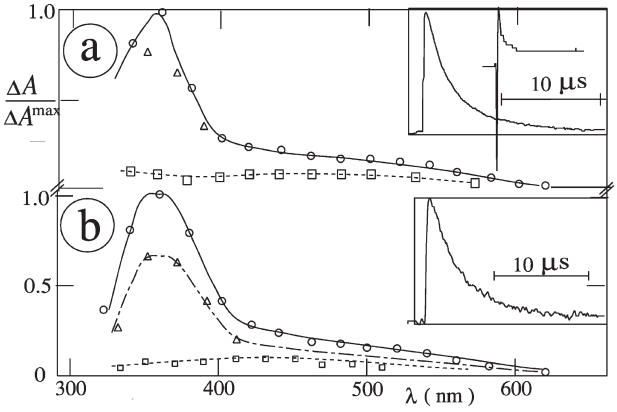


FIGURE 3. Transient absorption spectra in argon-saturated cyclohexane of (a) **2** and (b) **5** at 20 ns (○), 1 μs (Δ) and 10 μs (□) after the 308 nm pulse. Insets: kinetics at 360 nm for (a) **2** (left) and **1** (right) and (b) **5**.

and the rate constant is typically $k_{12} = (0.3-2) \times 10^9$ M^{-1} s^{-1}. The lifetime values for **5** in oxygen-, air- and argon-saturated CH_3CN are τ_T = 0.12, 0.7, and 7 μs, respectively. This corresponds to $k_{12} = 0.9 \times 10^9$ M^{-1} s^{-1}. Those in CH_3CN-H_2O (3:1) are τ_T = 0.25, 1.0, and 6−9 μs, respectively. Concerning H-atom transfer from 2-propanol to triplet phthalimide,[27] we found a significant quenching of τ_T for **2**, **5**, **3**, and **6**.

The triplet energy transfer to phthalimides was also studied in the presence of acetone, acetophenone, and benzophenone as sensitizers. The triplet lifetime of acetophenone in CH_3CN becomes shorter with increasing the concentration of **1**. The rate constant is $k_{10} = 2 \times 10^9$ M^{-1} s^{-1}. Similar values were found for benzophenone, but the triplet and the ketyl radical species are overlapped too much for a quantitative assessment. The triplet state of **1** or **4** can also be observed on addition of 2−5% acetone, whereby the sensitizer absorbs more than 90% of the excitation pulse at 308 nm. Examples of the spectra and kinetics of **1** and **4** in CH_3CN are shown in Figures 5a and b, respectively. The triplet lifetimes of **1** and **4** in several solvents are in the 1−10 μs range (Table 5). To probe for an effect of viscosity, glycerol triacetate (GT) was used. The triplet yield of **1** in GT under argon is low but is enhanced on addition of acetone (1−5%). The acetone-sensitized triplet lifetime in GT is significantly longer than in CH_3CN. The conclusion is that a higher viscosity increases the lifetime rather than the yield. A similar behavior was found for **4**.

Reaction Scheme. The direct and sensitized population of the lowest triplet state of phthalimides are steps 8 and 10. In the presence of a suitable donor, electron or H-atom transfer (11 or 11′, respectively) may occur, and these pathways are expected to be major photochemical processes, giving rise to photoproducts. The excited triplet state of phthalimides is known to undergo H-atom transfer from 2-propanol and electron transfer from donors such as amines. In principle, adamantane could serve as donor of an electron, or donor of a hydrogen atom. The measured rate constant for H-atom transfer from adamantane to triplet chloranil is $k_q = 1 \times 10^6$ M^{-1} s^{-1},[28] whereas the rate

(26) (a) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521–547. (b) Miranda, M. A.; Font-Sanchis, E.; Pérez-Prieto, J.; Scaiano, J. C. *J. Org. Chem.* **2001**, *66*, 2717–2721. (c) Font-Sanchis, E.; Miranda, M. A.; Pérez-Prieto, J.; Scaiano, J. C. *J. Org. Chem.* **2002**, *67*, 6131–6135.

(27) Samanta, A.; Ramachandram, B.; Saroja, G. *J. Photochem. Photobiol. A: Chem.* **1996**, *101*, 29–32.

(28) Mella, M.; Freccero, M.; Albini, A. *Tetrahedron* **1996**, *52*, 5549–5562.

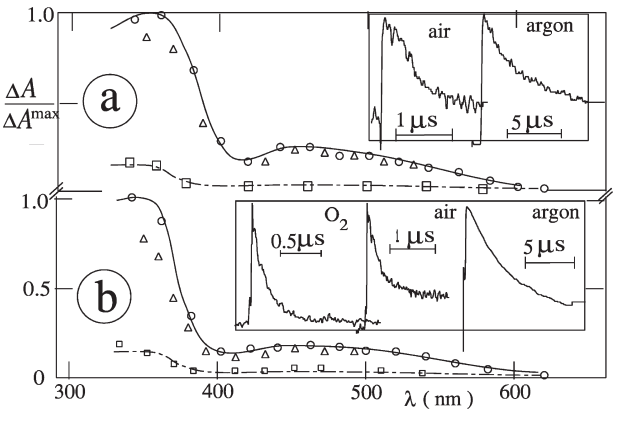


FIGURE 4. Transient absorption spectra of (a) **2** in argon-saturated CH_3CN and (b) **5** in CH_3CN-H_2O (3:1) at 20 ns (○), 1 μs (Δ) and 10 μs (□) after the 308 nm pulse. Insets: decay kinetics 360 nm under oxygen, air, and argon as indicated.

constant for the fluorescence quenching due to electron transfer from adamantane to singlet 1,2,4,5-benzenetetracarbonitrile (TCB) is $k_q = (0.2-1)\times 10^{10}\ M^{-1}\ s^{-1}$.[29] Additionally, quenching reactions of triplet states (12/12′) and radicals (13/13′) by oxygen have to be taken into account. The properties of the hydroperoxyl/superoxide ion-radical ($HO_2^{\bullet}/O_2^{\bullet -}$) are well-known.[30]

$$P + h\nu \rightarrow {}^{1*}P \rightarrow {}^{3*}P \quad (8)$$

$$S + h\nu \rightarrow {}^{1*}S \rightarrow {}^{3*}S \quad (9)$$

$${}^{3*}S + P \rightarrow S + {}^{3*}P \quad (10)$$

$${}^{3*}P + DH_2 \rightarrow P^{\bullet -} + DH_2^{\bullet +} \quad (11)$$

$${}^{3*}P + DH_2 \rightarrow PH^{\bullet} + DH^{\bullet} \quad (11')$$

$${}^{3*}P + O_2 \rightarrow P + O_2 \quad (12)$$

$${}^{3*}S + O_2 \rightarrow S + O_2 \quad (12')$$

$$P^{\bullet -} + O_2 \rightarrow P + O_2^{\bullet -} \quad (13)$$

$$PH^{\bullet} + O_2 \rightarrow P + HO_2^{\bullet} \quad (13')$$

Electron Transfer. As triplet quencher without formation of stable products in significant yield, DABCO was chosen. After reaction 11 back electron transfer is expected. On increasing the DABCO concentration, k_{obs} increases and the slope defines the rate constant of electron transfer k_{11}. The value is $k_{11} = 2\times 10^9\ M^{-1}\ s^{-1}$ of **2** or **5** in argon-saturated CH_3CN. Examples of **2**/DABCO in argon-saturated CH_3CN and CH_3CN-H_2O are shown in Figure 6a and b. The longer-lived transient with a maximum at 430 nm is attributed to the radical anion of the phthalimide moiety ($P^{\bullet -}$).

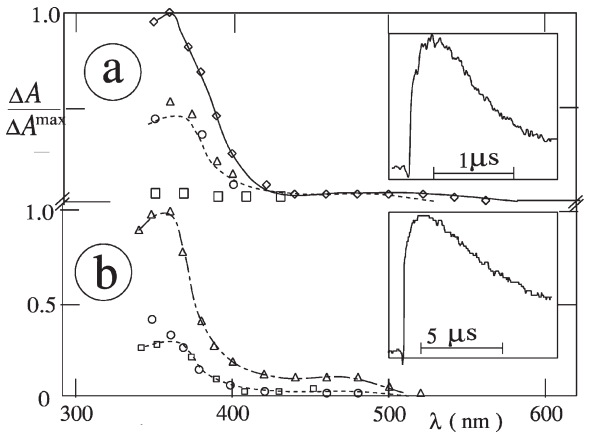


FIGURE 5. Transient absorption spectra in argon-saturated CH_3CN in the presence of 0.3 M acetone for (a) **1** and (b) **4** at 20 ns (○), 0.1 μs (◊), 1 μs (Δ) and 10 μs (□) after the 308 nm pulse. Insets: kinetics at 360 nm.

TABLE 4. Φ_{isc} Values of Phthalimides 1−8 in Several Solvents[a,b]

	Φ_{isc}			
compound	cyclohexane	CH_3CN	CH_3CN-H_2O (3:1)	TFE
1	< 0.01	< 0.01	0.01	< 0.01
2	0.3	0.4	0.5	0.3
3		0.4	0.4	
4	0.03	< 0.02	0.02	0.03
5	0.5	0.4	0.3	0.5
6		0.4	0.4	
7		0.5	0.6	
8		0.08	0.1	

[a] In argon-saturated solution, λ_{exc} = 308 nm. [b] Φ_{isc} = 0.8 for **9** in CH_3CN.

The triplet state can also be quenched by TEA, where photoreduction of the phthalimide moiety rather than back electron transfer is expected. Examples are shown in Figures 7a and b. The rate constant for **5** is $k_{11} = 5\times 10^9\ M^{-1}\ s^{-1}$. A similar value has been reported for **9**.[13d] The resulting radical anion is longer-lived ($t_{1/2} \sim 5$ ms) and quenched by oxygen, reaction 13, $k_{13} > 1\times 10^9\ M^{-1}\ s^{-1}$. When the TEA concentration is low enough not to affect triplet acetone, $P^{\bullet -}$ can be generated after energy transfer to $^{3*}P$, steps 10 and 11, as shown in Figure 7b for **4**.

Electrochemical Measurements. In agreement with earlier findings,[13,31] phthalimides **1**−**8** exhibit a reversible one-electron reduction at potentials that are correlated with the substituent at the imide nitrogen in the range of $E^{o\prime} = -1.89$ to −1.97 V vs Fc/Fc^+ (Table 6). The reduction of **1** and **8** occurs at the most negative potential (−1.97 V) of the whole series and can be explained by the strong inductive effect of the *tert*-alkyl substituent. The inductive effect is less pronounced for **4**; still the reduction of **4** is observed at a more negative potential than that of the less branched **7** used as a model compound. In the case of **3**, **5**, and **6** the inductive influence of the adamantyl group is negligible, resulting in almost identical reduction potentials equal to that of *N*-isobutylphthalimide.

(29) (a) Mella, M.; Freccero, M.; Albini, A. *Tetrahedron* **1996**, *52*, 5540–5562. (b) Mella, M.; Freccero, M.; Soldi, T.; Fasani, E.; Albini, A. *J. Org. Chem.* **1996**, *61*, 1413–1422. (c) Cardarelli, A. M.; Fagnoni, M.; Mella, M.; Albini, A. *J. Org. Chem.* **2001**, *66*, 7320–7327.

(30) (a) Cabelli, D. E.; Bielski, B. H. J. *J. Phys. Chem.* **1983**, *87*, 1809–1812. (b) von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor and Francis: London, 1987. (c) Cabelli, D. E. *The Reactions of HO2/O2- Radicals in Aqueous Solution*; Alfassi, Z. B., Ed.; Wiley: Chichester, 1997; pp 407.

(31) (a) Oelgemöller, M.; Griesbeck, A. G.; Lex, J.; Haeuseler, A.; Schmittel, M.; Niki, M.; Hesek, D.; Inoue, Y. *Org. Lett.* **2001**, *3*, 1593–1596. (b) Oelgemöller, M.; Haeuseler, A.; Schmittel, M.; Griesbeck, A. G.; Lex, J.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **2002**, 676–686.

TABLE 5. Triplet Lifetime (τ_T) of Phthalimides 1−8 in Several Solvents[a]

	τ_T (μs)				
compound	cyclohexane	GT[b]	CH_3CN	CH_3CN-H_2O (3:1)	TFE
1	0.4	(1−2)[c]	(0.9)[c]	(3)[c]	(4)[c]
2	3		3−6	4−6	20
3			4	7	
4		(12)[c]	(2−3)[c]		(5)[c]
5	9		4−6	6−9	9
6−8			5	8	

[a]In argon-saturated solution, λ_{exc} = 308 nm. [b]Glycerol triacetate. [c]In parentheses: acetone-sensitized.

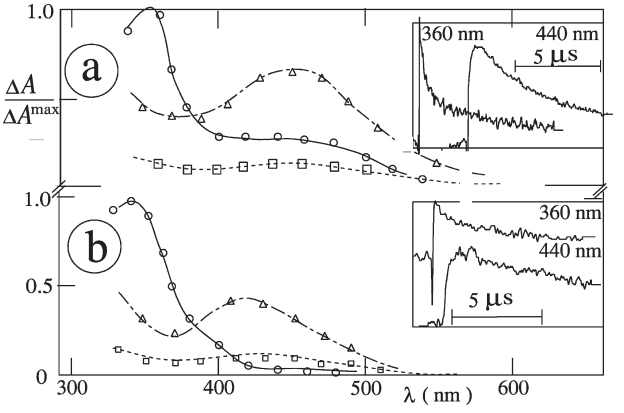


FIGURE 6. Transient absorption spectra of **2** in argon-saturated CH_3CN in the presence of (a) 2 mM DABCO and (b) 2 mM DABCO and 25% H_2O at 20 ns (o), 1 μs (Δ) and 10 μs (□) after the 308 nm pulse. Insets: kinetics at 360 nm (left) and 440 nm (right).

Oxidation of adamantane has been reported to occur at 2.72 V vs SCE.[29b] However, under our experimental conditions, a positive wave indicative for the oxidation of the adamantyl group could not be measured. The formation of the adamantyl radical cation as an intermediate has also been reported in PET reactions, with the excited singlet state of TCB as the oxidant. In the ground state in argon-purged CH_3CN, the latter exhibits a reversible one-electron reduction at $E^{o\prime} = -1.06$ V vs Fc/Fc^+ (and a second one at −2.02 V). Together with a singlet energy of 3.83 eV,[32] the excited singlet state reduction potential of TCB calculates to a value as high as 2.77 V. On the other hand, taking the triplet energy of 293 kJ mol^{-1} (3.0 eV) of **9** as a measure,[13] the reduction potential of the triplet excited state of **5** only sums up to 1.10 V vs Fc/Fc^+. While PET between the excited state of TCB and adamantane as a σ-donor is feasible, a similar process can be ruled out for the excited phthalimide chromophore. Consequently, all cyclization products identified must originate from other pathways, namely, intramolecular H-abstraction reactions.

Discussion

From the above results a reaction mechanism for the photochemical transformations of adamantyl phthalimides **1**−**6** is elucidated. Fluorescence properties were taken into consideration to test for singlet reactivity. Fluorescence of **1**−**6** is generally very weak (Table 3), and in accord with

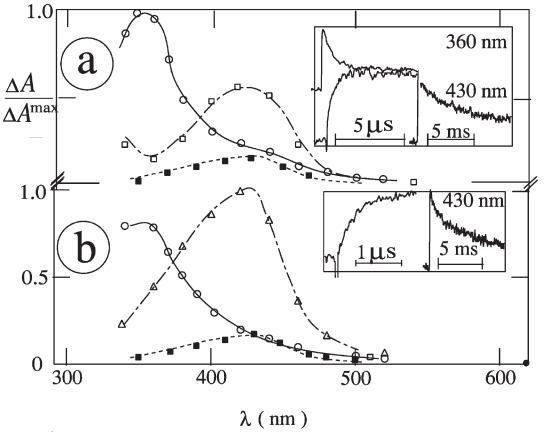


FIGURE 7. Absorption spectra in argon-saturated acetonitrile in the presence of 0.02 M TEA of (a) **5** and (b) **4** plus 0.3 M acetone at 20 ns (o), 1 μs (Δ), 10 μs (□) and 10 ms (■) after the 308 nm pulse. Insets: kinetics at 360 nm (left) and 430 nm (right).

TABLE 6. $E^{o\prime}$ Values of Phthalimides 1−8

compound	$E^{o\prime}$ (V)[a]
1	−1.97
2	−1.91
3	−1.90
4	−1.94
5	−1.90
6	−1.89
7	−1.92
8	−1.97

[a]The values $E^{o\prime}$ are referred vs Fc/Fc^+ as a reference electrode.

previous reports for the fluorescence of *N*-alkylphthalimides, Φ_f increases with polarity and H-bonding ability of the solvent.[12,13] Although the reports on energy levels of the excited states of the phthalimide chromophore are controversal,[12,13] the influence of solvent can be best explained by a switching of the energy levels in the singlet, as well as in the triplet manifolds. Most probably in polar protic solvents the fluorescent state S_1 is not $^1(n\pi^*)$ but the $^1(\pi\pi^*)$ state.[12e,13a] Furthermore, in a recent paper Kubo at al. discussed photophysical properties of *N*-alkylimides that are influenced by H-donor solvents.[33] They proposed an energy diagram in which $^1(\pi\pi^*)$ and $^3(n\pi^*)$ levels are close together, which is also in agreement with the energy diagram for the *N*-phthaloylvaline methyl ester.[13a] Increasing the solvent polarity and H-bonding ability both stabilizes ($\pi\pi^*$) and destabilizes ($n\pi^*$) states. Consequently, Φ_f increases, and Φ_{isc} decreases. However, it should also be recalled that the fluorescence lifetime (τ_f) of **9** in CH_3CN is as short as $\tau_f = 0.2$ ns,[12g] that is, any reaction originating from that state has to be extremely fast.

The major deactivation channel of *N*-alkylphthalimides after direct excitation is generally intersystem crossing to the triplet state.[13a] Therefore the triplet properties of phthalimides **1**−**8** were examined (Figures 3−7, Tables 4 and 5). However, for some adamantane derivatives (**1**, **4**, and *tert*-butyl derivative **8**) the measured Φ_{isc} is surprisingly low (Table 4). Direct or acetone-sensitized excitation, however, gave rise to transients that were assigned to the lower excited triplet $^3(\pi\pi^*)$ state of the phthalimides ($^{3*}P$) with associated

(32) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461–466.

(33) Matsubayashi, K.; Kubo, Y. *J. Org. Chem.* **2008**, *73*, 4915–4919.

TABLE 7. Comparison of Φ_{pr}^{rel} and Φ_{isc} of Phthalimides 1−6 in Polar Solvents

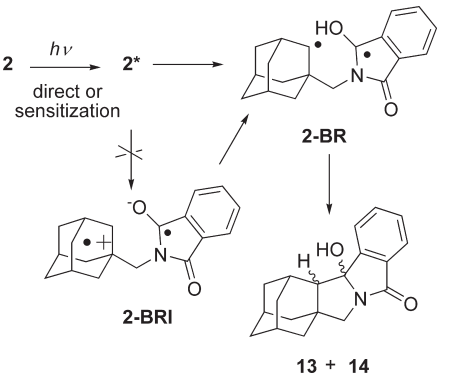
compound	solvent	Φ_d^{rel} [a]	Φ_{pr}^{rel} [b]	Φ_{isc} [c]
1	CH_3CN	< 0.01	< 0.03	< 0.01
	CH_3CN-H_2O (3:1)	0.01	0.03	0.01
2	CH_3CN	0.2	0.06	0.4
3	CH_3CN	0.4	0.3	0.4
	CH_3CN-H_2O (3:1)	0.8	1	0.4
4	CH_3CN	0.02	0.03	0.02
5	CH_3CN	0.4	0.4	0.4
	CH_3CN-H_2O (3:1)	1	1[d] (0.5)[e]	0.5
6	CH_3CN	0.4	0.6	0.4
	CH_3CN-H_2O (3:1)	1	0.7	0.4

[a]Taken from Table 2 and normalized. [b]The conversion is taken from Table 1 and normalized, $\Phi_{pr}^{rel} = 1$, using 30%/h for **3** in CH_3CN-H_2O (3:1). [c]Using Φ_{isc} from Table 4. [d]Absolute $\Phi_{pr} = 0.008$. [e]Oxygen-saturated.

lifetimes in the microsecond time scale. These transients were efficiently quenched by amines and oxygen. On the other hand, photochemical reactions of phthalimides **1**−**6** (Φ_d and Φ_{pr}) were very weakly quenched by oxygen, and the photoreaction of **5** was not quenched by DABCO.

Reaction Mechanisms. Before discussing reaction mechanisms it is informative to compare the results from conversion of synthetic and spectroscopic data (Table 7). Generally, Φ_d and Φ_{pr}^{rel} coincide. Why is the formation of product **23** from **5** so efficient in oxygen-saturated CH_3CN? The lowest triplet excited state as precursor has to be excluded on the basis of the lifetimes (see Figure 4b) and quenching studies. The surprising consequence could be (I) a singlet reaction or (II) a pathway via a hidden upper excited triplet. Although photochemical reactions from higher triplet states are rare, they have been reported.[13a,34] The comparison of data in Table 7 (Φ_{pr}^{rel} and Φ_{isc}) suggests that reactions proceed via a singlet excited state, pathway (I). Short fluorescence lifetimes τ_f do not contradict with route (I), since photoreactions of phthalimides are intramolecular. However, route (I) is not supported by the pattern of Φ_f values (Table 3), because Φ_f is large for **2**, **3**, **5** and **6**, where Φ_d is also large. Nevertheless, it cannot be excluded, since at most 1% of the excited molecules are involved in the product pathway. On the other hand, a strong argument in support of the upper triplet pathway (II) is the finding that the same products are obtained on direct and sensitized excitation of **1**, **4** and **5**. Moreover, a quenching study of the photoreaction of **5** with biacetyl also suggests route (II) and intermediacy of the upper triplet excited state. The quenching allowed for an estimation of the upper limit for the T_2 lifetime of 17 ns. The lifetimes of upper triplet excited states were reported to have values in the range of several tens of picoseconds[35] to 1 ns.[36]

SCHEME 1



After direct excitation of phthalimides in polar protic solvents, $^1(\pi\pi^*)$ is populated, which (more or less efficiently) undergoes ISC and populates the T_2 state. Thus, under direct excitation, photochemical reactions can probably take place via both pathways (I) and (II). On the other hand, in sensitized irradiations in which sensitizers with sufficient energy are used, the T_2 states are directly populated and photoreactions proceed only via pathway (II). For *N*-phthaloylvalin methyl ester, where Φ_d is much larger, involvement of an upper excited triplet state has been suggested.[13a] The next step in the reaction mechanism is an intramolecular H-atom abstraction from the adamantane or alkyladamantane part to the excited phthalimide, giving rise to biradical intermediates (Scheme 1). The other plausible mechanism, which would include an electron transfer from the adamantyl part to the excited phthalimide, is highly unlikely and most probably does not take place due to thermodynamic reasons (vide supra). Finally, the major products are formed via cyclization.

Remarkably, the quantum yield (i.e., % conversion per time) of **1** in acetone is relatively large and 3-fold enhanced in the presence of 25% water, being the same (absolute $\Phi_{pr} \sim 0.01$) as for **5** in CH_3CN-H_2O (see Table 1). This is attributed to a pathway involving triplet energy transfer. Such a route is also indicated for **4** in dry acetone ($\Phi_{pr} = 0.005$), in contrast to **2** in CH_3CN. The enhanced Φ_{pr} on addition of H_2O to CH_3CN suggests a step via water or proton assisted H-atom transfer. Alternatively, pronounced differences in photochemical reactivity depending on the polarity and the H-bonding ability of solvents could probably also be ascribed to different stabilization, and hence population of the excited singlet and triplet ($n\pi^*$) and ($\pi\pi^*$) states.

Formation of **13**−**15** in the photoreaction of **2** could be rationalized by an intramolecular H-abstraction of the adamantane H-atom by the excited phthalimide. Subsequent 1,5-biradical cyclization gave products **13** and **14**, which on loss of water gave **15**. Formation of the minor product **16** could probably be ascribed to a bimolecular process of H-atom abstraction by the excited phthalimide, followed by a trapping of the adamantane radical by oxygen.

In the photoreaction of **3**, the minor product **17** is probably formed in an intramolecular ε-H abstraction by the excited triplet state of the phthalimide **3**, followed by a biradical cyclization and a loss of water. ε-H abstractions are rare, especially when they are in competition with γ- abstractions.[37]

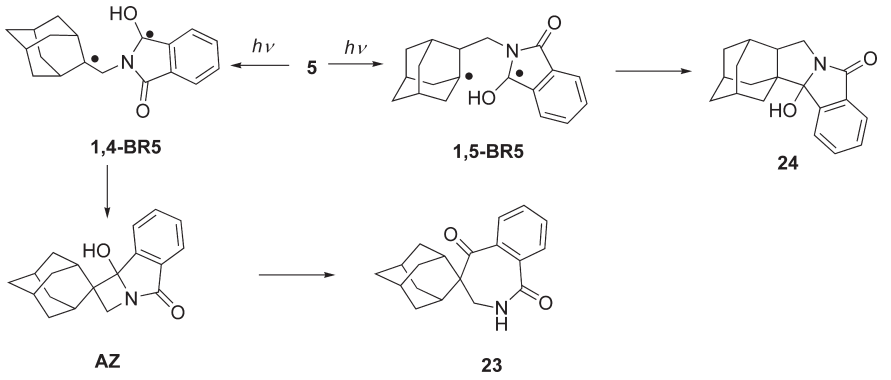
(34) (a) Zimmerman, H. E.; Amick, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3977–3982. (b) Demuth, M.; Amrein, W.; Bender, C. O.; Braslavsky, S. E.; Burger, U.; George, M. V.; Lemmer, D.; Schaffner, K. *Tetrahedron* **1981**, *37*, 3245–3261. (c) Schuster, D. I.; Calcaterra, L. T. *J. Am. Chem. Soc.* **1982**, *104*, 6397–6405. (d) Sadler, D. E.; Wendler, J.; Olbrich, G.; Schaffner, K. *J. Am. Chem. Soc.* **1984**, *106*, 2064–2071. (e) Wang, Z.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem.* **1993**, *97*, 374–378. (f) Encinas, S.; Miranda, M. A.; Marconi, G.; Monti, S. *Photochem. Photobiol.* **1998**, *67*, 420–425.

(35) (a) Bohne, C.; Kenedy, S. R.; Boch, R.; Negri, F.; Orlandi, G.; Siebrand, W.; Scaiano, J. C. *J. Phys. Chem.* **1991**, *95*, 10300–10306. (b) Sakamoto, M.; Cai, X.; Hara, M.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 9709–9714. (c) Cai, X.; Sakamoto, M.; Fujitsuka, M.; Majima, T. *Chem. Eur. J.* **2005**, *11*, 6471–6477. (d) Sakamoto, M.; Cai X.; Hara, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2005**, *109*, 4657–4661.

(36) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2004**, *108*, 9361–9364.

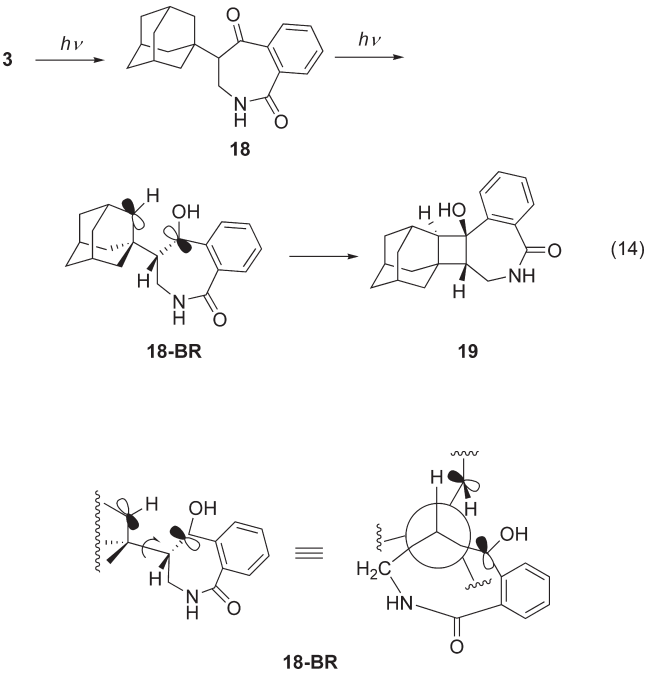
(37) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–177.

SCHEME 2



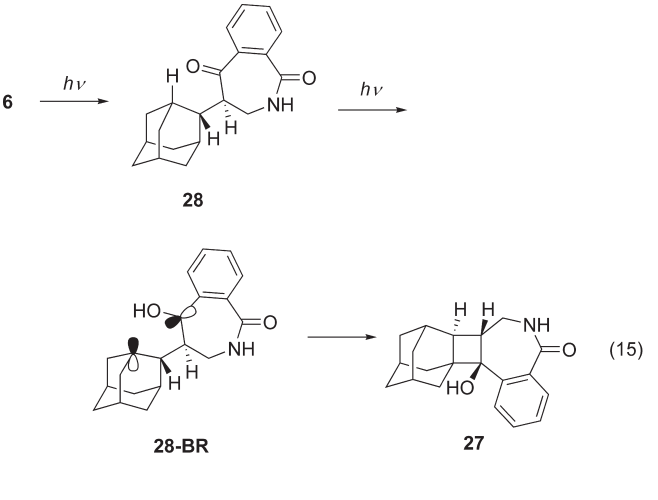
However, in this case it is probably taking place from a less stable conformer due to relatively restricted molecular motion caused by the bulky adamantane substituent. The formation of product **19** is rationalized by a domino sequence of two intramolecular photochemical H-abstractions. The first abstraction of γ-H atom gave rise to azetidinole intermediate (analogous to eq 1), which opened to amidoketone **18**. The second intramolecular photochemical γ-H atom abstraction gave biradical **18-BR**, which cyclized to domino product **19** (eq 14). The isolation of product **18** and its photochemical transformation to **19** strongly corroborates the anticipated domino reaction sequence. It is interesting to note that only one domino product was formed. Namely, the cyclobutane bond forming in **18-BR** could take place in two ways. The orbitals at the radical centers at azepinone and adamantane can overlap by an approach from the front or the rear side.

However, the first approach gives rise to the isolated product **19**, whereas the other possibility would result in the diastereomer (two hydrogens in a *cis* orientation and the OH group *trans*) that was not detected.



The formation of products in the photochemical reaction of **5** could be explained by the intramolecular δ- and γ-H abstractions. Whereas the γ-H abstraction results in a 1,4-biradical (**1,4-BR5**), which on cyclization gives azetidinol intermediate AZ and after ring enlargement spiro product **23**, the δ-H abstraction gives rise to 1,5-biradical (**1,5-BR5**), which on cyclization furnishes **24** (Scheme 2). Although γ-H abstractions are known to be much faster than δ-H abstractions,[37] in this case, δ-H is more available for abstraction due to the better geometrical arrangement to the phthalimide carbonyl.[11] Furthermore, since the 1-adamantyl radical is almost as stable as the 2-adamantyl radical (the energy difference is only 4 kJ mol^{-1}),[38] it is anticipated that **1,4-BR5**, which corresponds to a 2-adamantyl radical stabilized by an additional alkyl group, is more stable than **1,5-BR5**.

The mechanism of the photochemical transformation of **6** can be understood in view of intramolecular γ-, δ-, and ε-H abstractions. Whereas product **25** is formed via ε-H abstraction and 1,6-biradical closure, product **26** results from δ-H abstraction and 1,5-biradical closure. The azepinone derivative **27** is formed in a domino reaction sequence of two photoinduced intramolecular γ-H abstractions via intermediate ketoamide **28** (eq 15). The second photochemical reaction of **28** is stereospecific, resulting in only one diastereomer **27**. Examination of the structure of the intermediate biradical **28-BR** clearly indicates that it can cyclize only to one possible diastereomer **27**.



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Conclusions

N-Adamantyl- and *N*-(adamantylalkyl)phthalimides **1**−**6** undergo photochemical reactions on direct and sensitized irradiation. Product formation is explained by intramolecular γ-, δ-, or ε-H atom abstraction from the (alkyl)adamantane moiety by an excited state of the phthalimide. The alternative mechanism, which includes single electron transfer from the adamantyl part to the excited phthalimide, is highly unlikely due to thermodynamic reasons. On direct excitation, H-abstraction results from the singlet or an upper excited triplet state, as concluded from product yields in the presence and absence of oxygen. Besides the primary products that result from the initial photochemical H-abstraction and the C−C bond formation, two families of products were isolated. These are the products of the thermal domino reaction that follows the first photochemical step, or the products that result from three consecutive steps: photochemical (I), thermal, and photochemical (II). The latter were formed from phthalimide derivatives **1**, **3**, and **6**. Products of the thermal and the photochemical domino reactions are highly complex polycyclic benzazepines, for which tedious multistep conventional thermal synthesis would be required. Consequently, photoinitiated domino reactions are a useful synthetic tool for the formation of complex polycyclic structures.

Experimental Section

Photophysical Measurements. The UV absorption spectra were recorded on a diode array spectrophotometer. For photoconversion the 313 nm line of a Hg lamp and a filter were used. Alternatively, irradiation was performed with a 1000 W Xe−Hg lamp and a monochromator. The increase of absorption at the minimum around 255 nm was taken as a measure of conversion; the slope as a function of time defines a relative quantum yield, keeping the absorbance at $\lambda_{irr} = 313$ nm constant. Alternatively, Φ_{pr}^{rel} of conversion to products was used. The molar absorption coefficient of **9** is $\varepsilon_{295} = 1.4\times10^3\ M^{-1}\ cm^{-1}$. Irradiation of phthalimides in CH_3CN-H_2O (3:1) at pH 11 could not be carried out because of a thermal ring opening.[12] This also excludes long-time irradiation in the presence of TEA, in contrast to DABCO. In a few cases HPLC was used. The solutions were purged with argon prior to and during irradiation. The quantum yield was determined using *N*-phthalyltranexamic acid in argon-saturated acetonitrile, $\Phi_d = 0.2$.[13]

A spectrofluorimeter was employed to measure the fluorescence spectra. The yield was obtained using optically matched solutions and **9** in CH_3CN as reference, $\Phi_f = 0.0006$.[13a] An excimer laser provided 20 ns pulses at 308 nm (energy < 100 mJ). For **9** and 2-isobutylisoindoline-1,3-dione the quantum yield of intersystem crossing Φ_{isc} is 0.8 and 0.5, respectively.[13a] The transient absorption signals were measured with digitizers. The yields were obtained using optically matched solutions and **9** in CH_3CN as reference. As molar absorption coefficient of triplet benzophenone in acetonitrile, $\varepsilon_{525} = 6\times10^3\ M^{-1}\ cm^{-1}$ was taken. All measurements refer to 24 °C.

Electrochemical Measurements. These studies were performed in an air-tight cell under argon atmosphere in anhydrous CH_3CN with tetrabutylammonium hexafluorophosphate, NBu_4PF_6, as the supporting electrolyte at room temperature, using a potentiostat with a 0.01 N $AgNO_3$/Ag in CH_3CN as reference electrode. Two glassy carbon disk electrodes embedded in an insulating polymer were used as working and counter electrode, respectively. Reversibility of the phthalimide reduction was determined by examination of the forward and reverse peak currents at different scan rates between 50 mV s^{-1} and 1.6 V s^{-1}. The formal potentials ($E^{o\prime}$) are given as $E^{o\prime}$ (Fc/Fc^+) vs the ferrocene/ferricenium reference redox couple.[31]

2-Azapentacyclo[9.6.0.11,14.112,16.04,9]undeca-4,6,8-triene-3,10-dione (11). In a flask (50 mL), methanoadamantane **12** (207 mg, 0,736 mmol) was suspended in a mixture containing an aqueous solution of NaOH (20 mL, 10%) and EtOH (10 mL). The mixture was heated at the temperature of reflux for 10 min. From the cooled mixture, EtOH was removed on a rotary evaporator, and extraction with CH_2Cl_2 was carried out (3 × 20 mL). The extracts were dried over $MgSO_4$ and filtered, and the solvent was removed to afford a crude product that was additionally purified on a thin layer of silica gel using CH_2Cl_2−MeOH (5%) to afford pure product (56 mg, 27%). Colorless crystals, mp 283−285 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.96 (d, 1H, $J = 7.1$ Hz), 7.71 (dd, 1H, $J = 7.1$ Hz, $J = 1.7$ Hz), 7.67−7.57 (m, 2H), 6.61 (br s, 1H, NH), 3.03 (br s, 1H), 2.76 (br s, 1H), 2.21 (br s, 1H), 2.06 (dd, 1H, $J = 11.3$ Hz, $J = 2.6$ Hz), 1.94−1.81 (m, 5H), 1.70−1.64 (m, 2H), 1.53−1.45 (m, 2H), 1.34 (d, 1H, $J = 13.5$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 205.4 (s), 168.8 (s), 132.5 (d), 132.0 (d), 130.1 (d), 128.5 (d), 64.5 (d), 49.8 (s), 44.8 (t), 38.6 (t), 36.9 (t), 35.8 (t), 35.7 (d), 31.4 (t), 28.8 (d, 2C), two singlets were not seen; IR (KBr) ν 3438 (NH), 2921 (CH), 2851 (CH), 1671 (CO), 1649 (CO), 1408, 1279 cm^{-1}.

Photochemistry of 2-Azapentacyclo[9.6.0.1^{1,14}.1^{12,16}.0^{4,9}]undeca-4,6,8-triene-3,10-dione (11). In a quartz NMR tube, compound **11** (3 mg, 10.6×10^{-3} mmol) was dissolved in CD_3CN-D_2O (3:1, 1 mL). The solution was purged with argon for 10 min and irradiated at 300 nm in a Rayonet reactor for 20 min. After the irradiation the ^{1}H NMR spectrum was taken and showed the presence of only compound **12**.

Semipreparative Irradiations. General Procedure. *N*-(Adamantylalkyl)phthalimide (**1**−**6**, 100 mg) was dissolved in appropriate solvent (200 mL) and irradiated at 300 nm. During irradiation the solution was continuously purged with Ar and cooled by water. After irradiation, the solvent was evaporated on a rotary evaporator, and the residue was chromatographed on a column filled with silica gel using CH_2Cl_2−MeOH (up to 10%) as eluent.

Photochemistry of *N*-(1-Adamantylmethyl)phthalimide (2). *N*-(1-Adamantylmethyl)phthalimide (**2**, 600 mg 2.03 mmol) in CH_3CN (1 L, $c = 2.03\times10^{-3}$ M) was irradiated at 300 nm for 8 h. The residue, after evaporation of the solvent, was chromatographed on a column filled with silica gel using CH_2Cl_2−MeOH (10%) as eluent. In the first fraction 500 mg (83%) of the phthalimide **2** was isolated, followed by a mixture (80 mg) of the photochemical products, which were separated by repeated chromatography on a thin layer of silica gel using CH_2Cl_2−MeOH (2%) and $CH_2Cl_2-Et_2O$ (20%) as eluents.

***rel*-(11*S*,12*R*)-3-Aza-10-hydroxyhexacyclo[10.6.0.1^{1,15}.1^{13,17}.0^{3,11}.0^{5,10}]eicosa-5,7,9-triene-4-one (13).** Yield 20 mg (3.3%); colorless crystals (acetone), mp 180−185 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.65 (d, 1H, $J = 7.4$ Hz), 7.54−7.58 (m, 2H), 7.46 (dd, 1H, $J = 7.4$ Hz, $J = 7.8$ Hz), 3.23 (d, 1H, $J =$ 11.1 Hz,), 3.13 (d, 1H, $J = 11.1$ Hz), 2.89 (br s, 1H, OH), 2.78 (d, 1H, $J = 11.9$ Hz), 2.55 (d, 1H, $J = 12.2$ Hz), 2.46 (br s, 1H), 2.04 (br s, 1H), 2.02 (br s, 1H), 1.91 (d, 1H, $J = 11.6$ Hz), 1.82 (d, 1H, J = 12.5 Hz), 1.75 (d, 1H, $J = 12.2$ Hz), 1.69 (d, 1H, $J = 12.2$ Hz), 1.61−1.65 (m, 2H), 1.54−1.62 (m, 2H), 1.51 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 172.0 (s), 148.6 (s), 132.6 (d), 131.2 (s), 129.5 (d), 123.7 (d), 122.2 (d), 97.7 (s), 55.6 (t), 54.8 (d), 44.2 (t), 39.8 (t), 39.7 (t), 38.8 (s), 37.3 (t), 31.5 (t), 29.6 (d), 28.7 (d), 28.2 (d); IR (KBr) ν 3188 (OH), 2898 (CH), 2882 (CH), 1680 (CO) cm^{-1}.

***rel*-(11*S*,12*S*)-3-Aza-10-hydroxyhexacyclo[10.6.0.1^{1,15}.1^{13,17}.0^{3,11}.0^{5,10}]eicosa-5,7,9-triene-4-one (14).** Yield 50 mg (8.3%); colorless crystals (acetone), mp 252−253 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.77 (d, 1H, $J = 7.5$ Hz), 7.58 (ddd,

1H, $J = 1.0$ Hz, $J = 7.0$ Hz, $J = 7.5$ Hz), 7.55 (d, 1H, $J = 7.0$ Hz), 7.50 (dt, 1H, $J = 1.0$ Hz, $J = 7.5$ Hz), 3.66 (d, 1H $J = 11.1$ Hz), 3.02 (d, 1H $J = 11.1$ Hz), 2.64 (s, 1H, OH), 2.56 (br s, 1H), 2.52 (br s, 1H), 2.03 (br s, 1H), 1.82−1.88 (m, 2H), 1.79 (dd, 1H, $J = 2.0$ Hz, $J = 11.9$ Hz), 1.75 (d, 1H, $J = 11.9$ Hz), 1.61 (br s, 1H), 1.60 (d, 1H, $J = 12.0$ Hz), 1.55 (d, 1H, $J = 12.0$ Hz), 1.32 (d, 1H, $J = 12.6$ Hz), 1.22 (d, 1H, $J = 12.6$ Hz), 0.95 (d, 1H, $J = 12.6$ Hz), 0.89 (dd, 1H, $J = 2.0$ Hz, $J = 12.6$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 173.0 (s), 147.8 (s), 132.8 (d), 132.4 (s), 129.8 (d), 124.5 (d), 123.3 (d), 96.4 (s), 57.3 (d), 55.5 (t), 43.6 (s), 41.3 (t), 39.8 (t), 36.9 (t), 35.0 (t), 30.7 (t), 28.4 (d), 27.4 (d), 27.4 (d); IR (KBr) ν 3284 (OH), 2918 (CH), 2849 (CH), 1685 (CO), 1673 (CO) cm^{-1}; MS (EI) m/z 296 (10, M$^+$), 295 (40, M$^+$), 136 (10), 135 (100); HRMS, calculated for $C_{19}H_{21}NO_2$ 295.1572, observed 295.157.

3-Aza-10-hydroxyhexacyclo[10.6.0.0^{1,15}.1^{13,17}.0^{3,11}.0^{5,10}]eicosa-5,7,9,11-tetraene-4-one (15). Yield 3 mg (0.5%); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.85 (d, 1H, $J = 7.6$ Hz), 7.64 (d, 1H, $J = 7.6$ Hz), 7.52 (dt, 1H, $J = 1.1$ Hz, $J = 7.6$ Hz), 7.43 (dt, 1H, $J = 1.1$ Hz, $J = 7.6$ Hz), 3.57 (s, 2H), 3.32 (br s, 1H), 2.19 (br s, 2H), 1.80−2.10 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 162.2 (s), 135.0 (s), 130.8 (s), 130.2 (d), 127.9 (d), 126.8 (s), 123.2 (d), 121.8 (d), 52.3 (t), 44.4 (t, 2C), 38.5 (t, 2C), 35.9 (s), 31.7 (d), 29.2 (d, 2C); MS (EI) m/z 278 (25, M$^+$), 277 (90, M$^+$), 234 (25), 221 (25), 220 (100); HRMS (MALDI), calculated for $C_{19}H_{19}NO$ + H 278.1539, observed 278.1549.

***N*-[1-(3-Hydroxyadamantyl)methyl]phthalimide (16).** Yield 7 mg (1.2%); colorless crystals (acetone), mp 175−178 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.83−7.87 (m, 2H), 7.71−7.75 (m, 2H), 3.47 (s, 2H), 2.21 (br s, 2H), 1.95 (br s, 1H, OH), 1.40−1.70 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 168.8 (s), 133.8 (d), 131.2 (s), 123.1 (d), 68.6 (s), 48.5 (t), 48.2 (t), 44.2 (t), 39.4 (t), 38.9 (s), 35.0 (d), 30.2 (d); IR (KBr) ν 3504 (OH), 2925 (CH), 1710 (CO) cm^{-1}; MS (EI) m/z 312 (20, M$^+$), 311 (90, M$^+$), 161 (40), 151 (100); HRMS, calculated for $C_{19}H_{21}NO_3$ 311.1521, observed 311.151.

Photochemistry of *N*-[2-(1-Adamantyl)ethyl]phthalimide (3). *N*-[2-(1-Adamantyl)ethyl]phthalimide (**3**, 437 mg, 1.41 mmol) was dissolved in CH_3CN-H_2O (3:1, 1 L, $c = 1.4\times10^{-3}$ M) and irradiated at 300 nm for 8 h. The residue after evaporation of the solvent was chromatographed on a column filled with silica gel using CH_2Cl_2−MeOH (5%) as eluent. In the first fraction 192 mg (44%) of the phthalimide **3** was isolated, followed by a mixture (288 mg) of the photochemical products, which were separated by repeated chromatography on a thin layer of silica gel using CH_2Cl_2−MeOH (5%).

4-Azahexacyclo[11.6.0.0^{1,16}.1^{14,18}.0^{4,12}.0^{6,11}]uneicosa-6,8,10,12-tetraene-5-one (17). Yield 2 mg (2%); colorless crystals, mp 143−145 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.88 (d, 1H, $J = 7.5$ Hz), 7.83 (d, 1H, $J = 7.9$ Hz), 7.51 (ddd, 1H, $J = 0.9$ Hz, $J = 7.5$ Hz, $J = 7.9$ Hz), 7.40 (t, 1H, $J = 7.5$ Hz), 3.77 (t, 2H, $J = 6.0$ Hz), 3.64 (br s, 1H), 2.15 (br s, 2H), 2.04 (dd, 2H, $J = 2.2$ Hz, $J = 12.2$ Hz), 1.94−1.85 (m, 6H), 1.77 (d, 2H, $J = 12.0$ Hz), 1.71 (t, 2H, $J = 6.0$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 165.0 (s), 135.4 (s), 135.2 (s), 131.1 (d), 127.4 (d), 124.7 (s), 123.2 (d), 122,6 (d), 45.7 (t, 2C), 38.9 (t, 2C), 36.5 (t), 36.2 (t), 35.4 (s), 34.4 (t), 32.8 (d), 28.4 (d, 2C), one singlet is not seen due to small quantity of the sample; IR (KBr) ν 2917, 2849,1693 cm^{-1}; HRMS (MALDI), calculated for $C_{20}H_{21}NO$ + H 292.1696, observed 292.1687.

6-(1-Adamantyl)-3,4-benzoazepine-2,5-dione (18). Yield 130 mg (30%); colorless crystals, mp 155−160 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.86 (dd, 1H, $J = 2.2$ Hz, $J = 6.7$ Hz), 7.62−7.57 (m, 2H), 7.42 (dd, 1H, $J = 2.2$ Hz, $J = 6.7$ Hz), 6.88 (br s, 1H, NH), 3.67 (ddd, 1H, $J = 5.1$, $J = 12.6$, $J = 14.7$ Hz), 3.48 (ddd, 1H, $J = 4.6$ Hz, $J = 7.3$ Hz, $J = 14.7$ Hz), 2.66 (dd, 1H, $J = 4.6$ Hz, $J = 12.6$ Hz), 1.97 (br s, 3H), 1.73−1.54 (m, 12 H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 206.2 (s), 171.3 (s), 140.6 (s), 132.2 (d), 131.0 (d), 130.5 (s), 128.8 (d), 127.0 (d), 66.6 (d), 44.6 (s), 40.4 (t, 3C), 38.8 (t), 36.5 (t, 3C), 28.5 (d, 3C); IR (KBr) ν 3351, 2903, 2845, 1680, 1662 cm^{-1}; HRMS (MALDI), calculated for $C_{20}H_{23}NO_2$ + H 310.1801, observed 310.1791.

***rel*-(2*S*,12*R*,13*R*)-4-Aza-12-hydroxyhexacyclo[11.6.0.0^{1,16}.1^{14,18}.0^{2,12}.0^{6,11}]uneicosa-6,8,10-triene-5-one (19).** Yield 130 mg (30%); colorless crystals, mp 305−306 °C; ^{1}H NMR (DMSO, 600 MHz, ppm) δ 8.09 (t, 1H, $J = 6.1$ Hz, NH), 7.58 (d, 1H, $J = 7.8$ Hz), 7.48 (t, 1H, $J = 7.8$ Hz), 7.34 (d, 1H, $J = 7.7$ Hz), 7.30 (t, 1H, $J = 7.7$ Hz), 5.52 (s, 1H, OH), 3.21 (ddd, 1H, $J = 6.1$ Hz, $J = 13.0$ Hz, $J = 13.9$ Hz), 2.96 (ddd, 1H, $J = 3.0$ Hz, $J = 6.1$ Hz, $J = 13.9$ Hz), 2.85 (d, 1H, $J = 11.6$ Hz), 2.45 (br s, 1H), 2.38 (br s, 1H), 2.29 (d, 1H, $J = 11.7$ Hz), 2.24 (dd, 1H, $J = 13.0$ Hz, $J = 3.0$ Hz), 1.94 (br s, 2H), 1.76 (d, 1H, $J = 10.5$ Hz), 1.72−1.63 (m, 6H), 1.50 (d, $J = 10.5$ Hz); ^{13}C NMR (DMSO, 150 MHz, ppm) δ 169.7 (s), 146.0 (s), 131.1 (d), 130.4 (s), 129.8 (d), 128.5 (d), 126.7 (d), 84.0 (s), 60.1 (d), 54.5 (d), 40.5 (t), 40.3 (t), 39.9 (t), 38.9 (t), 37.8 (t), 35.6 (s), 31.5 (t), 29.9 (d), 29.6 (d), 28.0 (d); IR (KBr) ν 3314, 3174, 2908, 2867, 2844, 1654 cm^{-1}; HRMS (MALDI), calculated for $C_{20}H_{23}NO_2$ + H 310.1801, observed 310.1786.

Photochemistry of 6-(1-Adamantyl)-3,4-benzoazepine-2,5-dione (18). In a quartz NMR tube, compound **18** (3 mg, 9.7×10^{-3} mmol) was dissolved in CD_3CN-H_2O (3:1, 1 mL). The solution was purged with argon for 10 min and irradiated at 300 nm for 40 min. After the irradiation ^{1}H NMR spectrum was taken and showed the presence of a 1:1 mixture of compound **18** and **19**.

Photochemistry of *N*-(2-Adamantylmethyl)phthalimide (5). *N*-(2-Adamantylmethyl)phthalimide (**5**, 100 mg, 0.338 mmol) was dissolved in CH_3CN-H_2O (3:1, 200 mL, $c = 1.7\times10^{-3}$ M) and irradiated at 300 nm for 2 h. The residue after evaporation of the solvent was chromatographed on a column filled with silica gel using CH_2Cl_2−MeOH (up to 10%) as eluent. In the first fraction 42 mg (42%) of the starting phthalimide **5** was isolated, followed by 50 mg (42%) of the photoproducts, which were separated by repeated chromatography on preparative TLC with CH_2Cl_2−MeOH (10%) as eluents.

Spiro[adamantane-2,6′-(3′,4′-benzoazepin-2′,5′-dione)] (23). Yield 42 mg (42%); colorless crystals, mp 221−223 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.96−7.93 (m, 1H), 7.59−7.54 (m, 2H), 7.34−7.26 (m, 1H), 6.47 (br s, 1H, NH), 3.59 (d, 1H), 2.36 (br s, 1H), 2.31 (s, 1H), 2.10 (br s, 2H), 1.95−1.90 (m, 4H), 1.74−1.69 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 207.0 (s), 170.1 (s), 139.0 (s), 131.0 (d), 129.4 (d), 128.1 (d), 124.9 (d), 58.2 (s), 46.0 (t), 37.4 (t), 33.1 (t, 2C), 32.2 (t, 2C), 30.1 (d, 2C), 26.4 (d), 26.2 (d); IR (KBr) ν 3193, 3080, 2895, 2863, 1678 cm^{-1}; MS (EI) m/z 295 (5, M$^+$), 266 (40), 148 (100); HRMS, calculated for $C_{19}H_{21}NO_2$ 295.1572, observed 295.157.

2-Methoxy-10-azahexacyclo[10.6.0.0^{1,15}.1^{13,17}.0^{2,10}.0^{3,8}]eicosa-3,5,7-triene-9-one (24). Yield 8 mg (8%); colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.77 (dd, 1H, $J = 7.5$ Hz, $J = 1.0$ Hz), 7.55 (ddd, 1H, $J = 7.4$ Hz, $J = 7.5$ Hz, $J = 1.0$ Hz), 7.48 (ddd, 1H, $J = 7.5$ Hz, $J = 7.4$ Hz, $J = 1.0$ Hz), 7.36 (dd, 1H, $J = 7.4$ Hz, $J = 1.0$ Hz), 3.50 (d, 1H, $J = 10.9$ Hz), 3.37 (dd, 1H, $J = 8.4$ Hz, $J = 10.9$ Hz), 2.98 (dd, 1H, $J = 8.4$ Hz, $J = 9.6$ Hz), 2.94 (s, 3H, OCH_3), 2.22 (ddd, 1H, $J = 2.5$ Hz, $J = 5.1$ Hz, $J = 11.9$ Hz), 2.10 (br s, 1H), 2.03 (br s, 1H), 1.85−1.82 (m, 2H), 1.76−1.75 (m, 3H), 1.69−1.65 (m, 1H), 1.58−1.52 (m, 2H), 0.77−0.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 171.8 (s), 142.0 (s), 134.8 (s), 132.0 (d), 129.5 (d), 123.5 (d), 122.6 (d), 103.1 (s), 50.1 (q), 48.8 (d), 44.1 (t), 43.2 (s), 38.0 (t), 37.2 (t), 35.8 (t), 33.5 (t), 30.7 (t), 28.4 (d, 2C), 27.4 (d); IR (KBr) ν 2906, 2852, 1709, 1356, 1347 cm^{-1}; MS (EI) m/z 310 (5, M$^+$), 309 (10, M$^+$), 295 (25), 294 (100), 160 (20), 147 (25); HRMS calculated for $C_{19}H_{23}NO_2$ 309.1729, observed 309.173.

Photochemistry of *N*-[2-(2-Adamantyl)ethyl]phthalimide (6). *N*-[2-(2-Adamantyl)ethyl]phthalimide (**6**, 100 mg, 0.323 mmol) was dissolved in CH_3CN-H_2O (3:1, 200 mL, $c = 1.6\times10^{-3}$ M) and irradiated at 300 nm for 2 h. The residue after evaporation of the solvent was chromatographed on a column filled with

silica gel using CH_2Cl_2−MeOH (5%) as eluent. In the first fraction 57 mg (57%) of the phthalimide **6** was isolated, followed by a mixture (43 mg) of the photochemical products, which were separated by repeated chromatography on a thin layer of silica gel using CH_2Cl_2−MeOH (5%).

***rel*-(2*R*,13*R*)-2-Hydroxy-10-azahexacyclo[11.6.0.1^{1,16}.1^{14,18}.0^{2,10}.0^{3,8}]uneicosa-3,5,7-triene-9-one (25).** Yield 4 mg (4%); colorless crystals, mp 151−153 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.61 (d, 1H, J = 7.5 Hz), 7,60 (d, 1H, J = 7.5 Hz), 7.50 (t, 1H, J = 7.5 Hz), 7.39 (t, 1H, J = 7.5 Hz), 4.13 (dd, 1H, J = 13.0 Hz, J = 5.5 Hz), 3,15 (dt, 1H, J = 13.0 Hz, J = 3.9 Hz), 2.37−2.32 (m, 2H), 2.10 (br s, 1H), 2.03 (dd, 1H, J = 12.2 Hz, J = 2.1 Hz), 1.92 (dddd, 1H, J = 13.5 Hz, J = 13.3 Hz, J = 5.5 Hz, J = 3.9 Hz), 1.85 (dd, 1H, J = 12.2 Hz, J = 2.2 Hz), 1.81 (ddd, 1H, J = 12.2 Hz, J = 4.5 Hz, J = 2.1 Hz), 1.78−1.68 (m, 3H), 1.63 (d, 1H, J = 12.4 Hz), 1.45 (d, 1H, J = 12.4 Hz), 1.41−1.39 (m, 2H), 1.35 (dd, 1H, J = 13.3 Hz, J = 3.9 Hz), 0.49 (d, 1H, J = 12.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 165.0 (s), 145.9 (s), 132.0 (s), 131.2 (d), 129.1 (d), 123.3 (d), 122.7 (d), 90.8 (s), 40.4 (s), 39.9 (d), 38.3 (t), 37.7 (t), 37.3 (t), 35.1 (t), 33.0 (d), 31.1 (t), 30.6 (t), 28.6 (d), 28.0 (d), 26.2 (t); IR (KBr) ν 3421, 2911, 1673 cm^{-1}; HRMS (MALDI), calculated for $C_{20}H_{23}NO_2$ + H 310.1801, observed 310.1796.

Spiro[adamantane-2,6′-(4′-aza-3′,4′-benzo-5′-hydroxybicyclo-[3.3.0]octane-2-one)] (26). Yield 10 mg (10%); colorless crystals, mp 181−185 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.80 (d, 1H, J = 7.8 Hz), 7.62 (d, 1H, J = 7.5 Hz), 7.55 (ddd, 1H, J = 7.6 Hz, J = 7.3 Hz, J = 1.1 Hz), 7.43 (ddd, 1H, J = 7.5 Hz, J = 7.6 Hz, J = 0.7 Hz), 3.47 (ddd, 1H, J = 11.2 Hz, J = 7.6 Hz, J = 3.3 Hz), 3.20 (dd, 1H, J = 11.2 Hz, J = 9.0 Hz), 2.71 (dd, 1H, J = 13.0 Hz, J = 7.6 Hz), 2.45−2.39 (m, 2H), 2.33 (br s, 1H), 2.07 (ddd, 1H, J = 13.2 Hz, J = 2.6 Hz, J = 2.5 Hz), 1.92 (ddd, 1H, J = 13.1 Hz, J = 2.6 Hz, J = 2.5 Hz), 1.82 (br s, 1H), 1.75 (ddd, 1H, J = 13.0 Hz, J = 5.1 Hz, J = 2.6 Hz), 1.71 (ddd, 1H, J = 13.1 Hz, J = 5.1 Hz, J = 2.6 Hz), 1.70−1.65 (m, 2H), 1.59 (ddd, 1H, J = 12.0 Hz, J = 2.2 Hz, J = 2.1 Hz), 1.50 (ddd, 1H, J = 13.2 Hz, J = 5.0 Hz, J = 2.5 Hz), 1.20 (br s, 1H), 1.06 (ddd, 1H, J = 13.2 Hz, J = 4.7 Hz, J = 2.3 Hz), 0.93 (ddd, 1H, J = 13.2 Hz, J = 5.2 Hz, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 169.2 (s), 147.7 (s), 132.9 (s), 132.0 (d), 129.3 (d), 125.7 (d), 123.3 (d), 99.5 (s), 54.6 (s), 39.2 (t), 37.6 (t), 36.9 (t), 34.9 (t), 34.2 (t), 34.0 (t), 33.0 (t), 32.6 (d), 28.9 (d), 27.3 (d), 27.2 (d); IR (KBr) ν 3421, 2918, 2859, 1685 cm^{-1}; HRMS (MALDI), calculated for $C_{20}H_{23}NO_2$ + H 310.1801, observed 310.1804.

***rel*-(2*R*,12*S*,13*S*)-2-Hydroxy-10-azahexacyclo[11.6.0.1^{1,16}.1^{14,18}.0^{2,12}.0^{3,8}]uneicosa-3,5,7-triene-9-one (27).** Yield 25 mg (25%); colorless crystals, mp 210−215 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.31 (br s, 1H, NH), 7.81 (dd, 1H, J = 7.0 Hz, J = 1.3 Hz), 7.71 (dd, 1H, J = 7.2 Hz, J = 1.1 Hz), 7.42−7.38 (m, 2H), 4.67 (br s, 1H, OH), 3.22 (ddd, 1H, J = 5.9 Hz, J = 6.1 Hz, J = 13.4 Hz), 2.97 (ddd, 1H, J = 5.2 Hz, J = 5.9 Hz, J = 10.9 Hz), 2.88 (ddd, 1H, J = 5.9 Hz, J = 11.6 Hz, J = 13.4 Hz), 2.39 (d, 1H, J = 10.3 Hz), 2.32 (d, 1H, J = 13.2 Hz), 2.22 (d, 1H, J = 10.3 Hz), 2.01 (br s, 1H), 1.96 (br s, 1H), 1.78−1.67 (m, 5H), 1.57 (d, 1H, J = 12.3 Hz), 1.44 (d, J = 10.9 Hz), 1.28 (d, 1H, J = 10.9 Hz), 1.25−1.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 173.3 (s), 140.3 (s), 136.2 (s), 131.1 (d), 130.0 (d), 127.7 (d), 127.5 (d), 83.3 (s), 53.5 (d), 45.9 (s), 44.4 (t), 44.2 (t), 43.6 (d), 39.4 (t), 37.6 (t), 35.1 (t), 30.9 (t), 30.7 (d), 27.9 (d, 2C); IR (KBr) ν 3421, 2905, 2852, 1649 cm^{-1}; MS (EI) m/z 310 (3, M$^+$), 309 (10, M$^+$), 281 (25), 280 (60), 264 (25), 252 (40), 162 (35), 148 (40), 146 (100), 130 (25), 105 (40), 91 (40), 79 (40), 77 (45); HRMS, calculated for $C_{20}H_{23}NO_2$ 309.1729, observed 309.173.

Quantum Yield of the Photochemical Reaction of *N*-(2-Adamantylmethyl)phthalimide (5). In two quartz cuvettes (20 mL) a solution of phthalimide **5** ($1.7 \times 10-3$ M) and a solution of valerophenone (6×10^{-4} M), respectively, in CH_3CN-H_2O (3:1) were purged with argon for 15 min and irradiated (at the same time) in a Rayonet reactor at 300 nm. The samples of the irradiated solution were taken after 1.5, 3, and 4.5 min, and the composition was analyzed by HPLC.

Quenching of the Photochemical Reaction of *N*-(2-Adamantylmethyl)phthalimide (5) with Biacetyl. Solutions of phthalimide **5** (1.7×10^{-3} M) in CH_3CN-H_2O (3:1) that contained biacetyl in concentrations of 0, 0.0057, 0.0114, 0.0171, 0.0228, 0.0285, and 0.0342 M, respectively, were placed in seven quartz cuvettes (20 mL). The solutions were purged with argon for 15 min and irradiated (at the same time) at 300 nm for 15 min. After the irradiation composition of the solutions was analyzed by HPLC.

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Supporting Information Available: General and detailed experimental procedure, physical characterization, ^{1}H NMR and ^{13}C NMR spectra of **13**−**19** and **23**−**27**, and crystallographic data for **14**, **19**, **23**, and **27**. This material is available free of charge via the Internet at http://pubs.acs.org.