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THE PHOTODECARBOXYLATIVE ADDITION OF CARBOXYLATES TO PHTHALIMIDES: SCOPE AND LIMITATIONS[#]

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Abstract – *Intermolecular* photoinduced decarboxylative additions of a series of alkylcarboxylates to *N*-substituted phthalimides gave the corresponding hydroxy-phthalimidines in moderate to high yields of 39-89%. The potassium salt of 1-adamantanecarboxylic acid predominately underwent *simple* decarboxylation when irradiated in the presence of *N*-methylphthalimide. In case of phthalimides carrying suitable leaving groups within the *N*-side chain, decarboxylation, retro-Aldol cleavage or decarbonylation preceded the *intermolecular* addition step.

INTRODUCTION

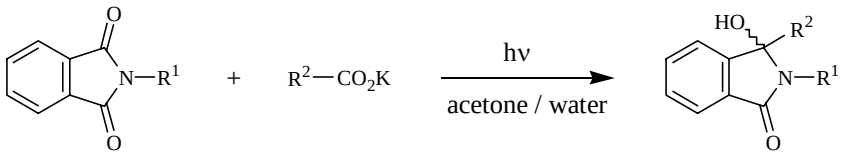
Since the pioneering work of Kanaoka and coworkers in the early 1970'ies,[1] the photochemistry of phthalimides has attracted growing attention in terms of synthetic organic photochemistry.[2] Among the numerous *intermolecular* applications, addition reactions of alkenes,[3] alcohols,[4] ethers,[3d,5] thioethers,[6] alkylbenzenes,[7] and amines[7b] to the phthalimide system have been reported. In many cases, however, these reactions gave poor yields, and mixtures of the desired photoaddition and photoreduction products were obtained. During our ongoing studies on *intramolecular* photodecarboxylative cyclization reactions of ω-phthalimidoalkylcarboxylates, we found that the alkylcarboxylate anion can be used as a powerful activating and directing group, and developed a suitable method for the synthesis of various macrocyclic systems in good to high yields.[8] As an extension of this concept, we have briefly described a corresponding *intermolecular* addition version leading to Grignard reaction-alike products.[9] To further explore the scope and limitation of this addition reaction, we have investigated several carboxylate/phthalimide systems in detail. An important aspect was a mild and convenient photochemical pathway to hydroxy-

[#] Dedicated to Prof. Yuichi Kanaoka on the occasion of his 75th birthday.

phthalimidines, which were previously commonly synthesized *via* thermal methods, *e.g.* SmI_2-mediated coupling of organic halides (SmI_2/R-X),[10a] addition of organometallic compounds (R-Mg-X or R-Li),[10b-d] or alkylation with organic halides using lithium in liquid ammonia (Li/NH_3/R-X),[10e] respectively.

RESULTS AND DISCUSSION

In a first series of experiments *N*-methylphthalimide (**1a**) was used as a model substrate and the carboxylate compound (**2a-i**) was varied. Upon irradiation in aqueous acetone and in the presence of 3-6 equivalents of the potassium carboxylate, the corresponding hydroxyphthalimidines (**3a-h**) were obtained in moderate to good yields of 39-89%. Solely potassium benzoate (**2i**) remained unreactive and *N*-methylphthalimide (**1a**) was reisolated in 86% yield even after prolonged irradiation. From the carboxylate (**2d**) a mixture of diastereoisomers with low *d.e.* of 10% was obtained. Other *N*-substituted phthalimides (**1b-e**) were investigated using potassium propionate (**2b**) as the alkylating reagent and similar hydroxy phthalimidines (**3j-m**) were obtained in yields of 52-88%. Unlike alternative thermal additions (*e.g.* Grignard reactions[10b,c]), other carbonyl groups as in substrates (**1d**) and (**1e**) were tolerated and photo-induced alkylation occurred regioselectively at the imide chromophore and not at the ester or amide carbonyl group. The general reaction is outlined in Scheme 1 and selected experimental details are summarized in Table 1.



1 **2** **3** (39-89%)

Scheme 1

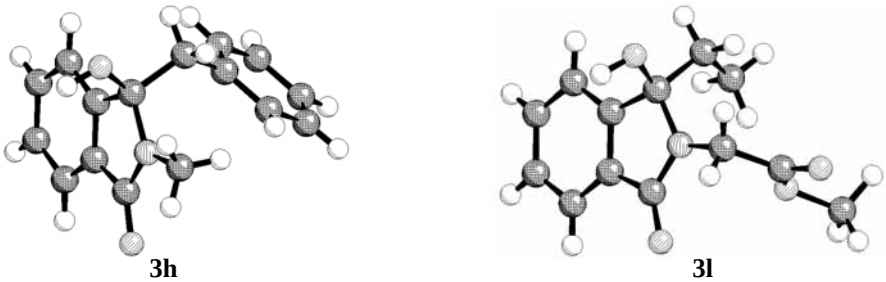
The reaction process was easily monitored by TLC analysis or by passing a stream of nitrogen gas through the reaction mixture and subsequently into a saturated barium hydroxide solution until precipitation of barium carbonate has ceased. Best results were obtained with 20% aqueous acetone as solvent and 5 equivalents of carboxylate. An excess amount of carboxylate was required in order to drive the reaction to high conversion. For most experiments, a Rayonet reactor equipped with mercury low pressure lamps (phosphor coated with an emission maximum at 300 nm; 800 W) was used but alternatively a high pressure mercury lamp (400 W) served as an efficient light source.

Recrystallization from acetone gave suitable crystals of **3h** and **3l** for X-Ray crystallographic analysis and the structures are shown in Figure 1.

Table 1 Photodecarboxylative additions of potassium carboxylates (**2**) to phthalimides (**1**).

Substrates				Conditions				Photoproduct	
1	$\mathbf{R^1}$ (amount [g])	**2**	$\mathbf{R^2}$ (amount [g])	acetone/ H_2O [mL]	light-source[a]	time [h]	conv. **1** [%][b]	**3**	yield **3** [%]
1a	Me (0.32)	**2a**	Me (1.0)	4:1 (200)	A	41	42	**3a**	39 (93[b])
1a	Me (0.36)	**2b**	Et (1.0)	9:1 (200)	A	23	100	**3b**	88
1a	Me (0.28)	**2c**	*i*-Pr (0.7)	9:1 (150)	A	23	100	**3c**	86
1a	Me (6.45)	**2c**	*i*-Pr (30.3)	1:3 (2000)	B	4 ¼	73	**3c**	63 (86[c])
1a	Me (0.32)	**2d**	*s*-Bu (1.4)	4:1 (300)	C	1 ½	100	**3d**	89 (10[d])
1a	Me (0.32)	**2e**	*i*-Bu (1.4)	4:1 (300)	C	1 ½	85	**3e**	51 (60[c])
1a	Me (0.32)	**2f**	*t*-Bu (1.4)	4:1 (300)	A	23	100	**3f**	57
1a	Me (0.32)	**2f**	*t*-Bu (1.4)	4:1 (300)	C	1	89	**3f**	76 (85[c])
1a	Me (0.22)	**2g**	CH_2-*t*-Bu (1.2)	9:1 (150)	A	23	100	**3g**	80
1a	Me (0.35)	**2h**	Bn (1.3)	9:1 (200)	A	20	100	**3h**	88
1a	Me (0.35)	**2i**	Ph (1.6)	9:1 (200)	A	48	0 (86[e])	**3i**	0
1b	Ph (0.45)	**2b**	Et (1.0)	4:1 (200)	A	24	60	**3j**	55 (92[c])
1c	$CH_2C{\equiv}CH$ (0.19)	**2b**	Et (0.6)	4:1 (300)	A	23	100	**3k**	88
1d	CH_2CO_2Me (0.41)	**2b**	Et (1.1)	4:1 (300)	A	17	100	**3l**	88
1e	$CH_2CONHCH_2CO_2Me$ (0.52)	**2b**	Et (1.0)	9:1 (200)	A	17	100	**3m**	52

[a] **A**: Rayonet (300 ± 10 nm); **B**: XeCl excimer (308 nm); **C**: High-pressure mercury lamp (400 W). [b] Determined by ^{1}H NMR spectroscopy or GC analysis of the crude product. [c] Yield based on conversion. [d] *d.e.* (*unlike*-/*like*-**3d**). [e] Reisolated **1**.

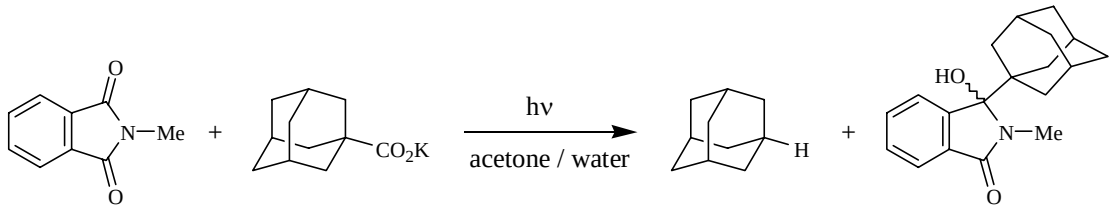


3h **3l**

Figure 1 Structures of **3h** and **3l** in the crystal.

As a side-reaction of the *intramolecular* cyclization version, the formation of *simple* decarboxylation products (CO_2^-/H-exchange) was commonly observed.[8] Similarly, *simple* decarboxylation was expected to compete with the addition reaction. From these side-reactions, volatile alkanes were expected to be formed which escaped from the reaction mixture and could not be detected after work-up. However, when the potassium salt of 1-adamantanecarboxylic acid (**2j**) was used the corresponding alkane adamantane (**4**) was isolated as main product in yields of 60-69%. Most of the *N*-methylphthalimide (**1a**)

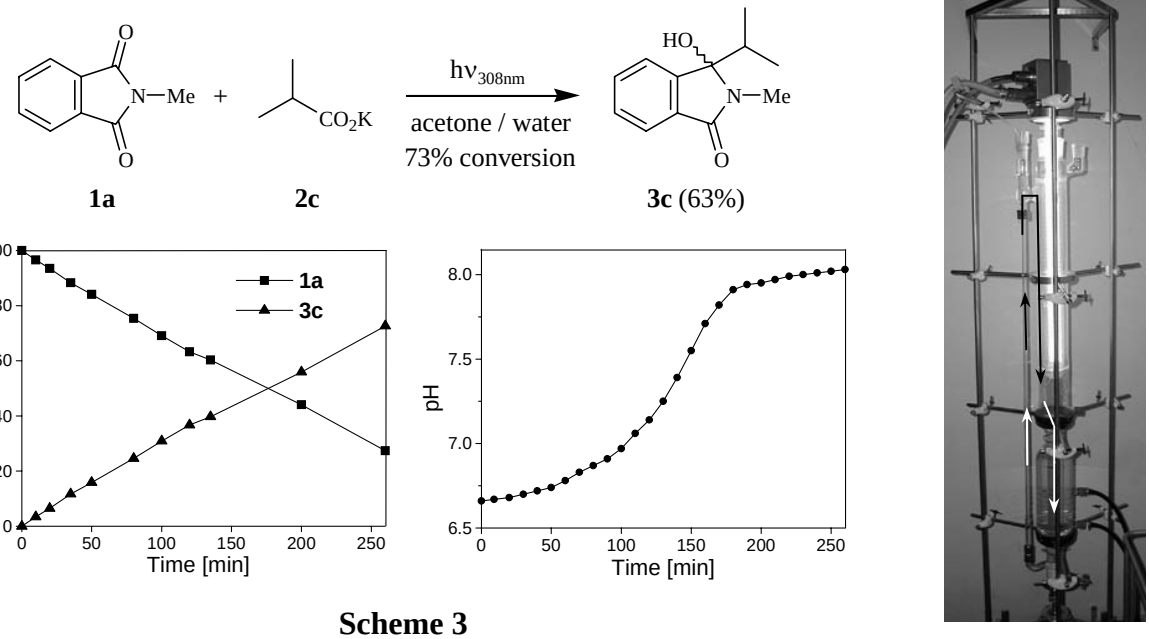
remained unchanged and could be reisolated. In one exemplary case **1a** and unreactive carboxylic acid were recovered in yields of 78% and 37%, respectively, whereas the photoaddition product (**3n**) was obtained in 2% yield next to 60% of **4**. Hence, in case of 1-adamantanecarboxylic acid the phthalimide acts as a catalyst for an *electron shuttle process*.



1a **2j** **4** (60-69%) **3n** (2%)

Scheme 2

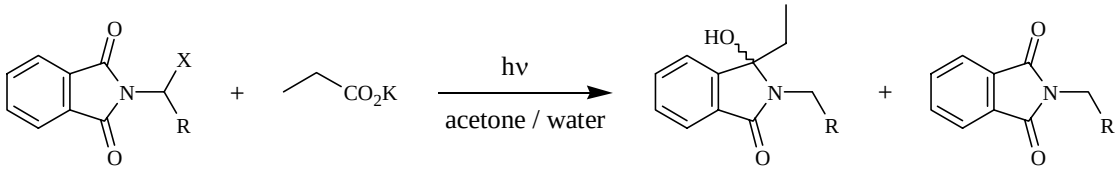
As a model reaction for a large scale preparation, the photodecarboxylative addition of potassium *iso*-butyrate (**2c**) to **1a** was performed using a falling-film apparatus equipped with a 308 nm XeCl excimer light source (Scheme 3).[11] This reaction proceeded smoothly on a multigram scale in a 3:1 (vol %) water-acetone mixture using 6 equivalents of the alkyl carboxylate and a 0.02 M solution of phthalimide (**1a**). The reaction progress was monitored by continuous pH control and gas chromatographic determination of the substrate/product ratio (**1a**/**3c**).



Scheme 3

The photoaddition protocol was furthermore expanded to phthalimides (**5**) carrying photochemically labile side-chains (indicated as **X**). In all cases examined, irradiation in the presence of potassium pro-

pionate (**2b**) led to cleavage of the photo-labile group prior to alkylation (Scheme 4; Table 2). These extrusion processes also occurred in the absence of carboxylate as proven by independent runs under similar conditions. However, the conversions were significantly lower for **5c** and **5e** in the latter cases. The phthaloylated α-amino acids (**5a**) and (**5b**) underwent rapid α-decarboxylation, a process originally discovered by Kanaoka and coworkers.[12] The phthalimidopropanol derivative (**5c**) showed retro-Aldol cleavage,[13] whereas decarbonylation or elimination of malonic acid diester preceded the photoinduced alkylation for phthalimides (**5d**) and (**5e**), respectively.



5a-e **2b** **3b,o** (33-93%) **1a,f**

Scheme 4

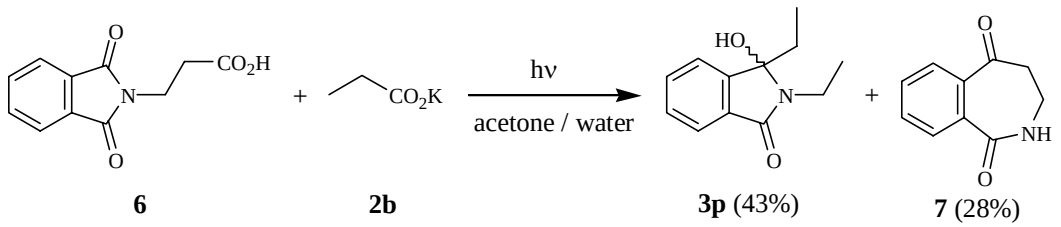
Table 2 Photoreactions involving phthalimides (**5a-e**).

Substrates					Conditions			Photoproducts	
5	**X**	**R**	**5** amount [g]	**2b** amount [g]	acetone/ H_2O [mL]	time [h]	conv. **5** [%][a]	yields [%]	
5a	CO_2H	H	0.41	0.57	1:1 (200)	31	100	33 (**3b**)	33 (**1a**)
5a	CO_2H	H	0.41	—[b]	1:1 (200)	23	100	—	89 (**1a**)
5b	CO_2H	Bn	0.5	1.0	9:1 (100)	26	100	67 (**3o**)	25 (**1f**)
5b	CO_2H	Bn	0.5	—[b]	1:1 (200)	24	100	—	90 (**1f**)
5c	CH(OH)Me	H	0.5	1.2	1:1 (300)	35	100	43 (**3b**)	27 (**1a**)
5c	CH(OH)Me	H	0.21	—[b]	4:1 (50)	24	5	—	n.d.[c] (**1a**)
5d	CHO	H	0.38	1.1	4:1 (300)	16	100	80 (**3b**)	—
5d	CHO	H	0.19	—[b]	4:1 (50)	24	100	—	96 (**1a**)
5e	$CH(CO_2Me)_2$	H	0.32	1.1	4:1 (300)	21	100	93 (**3b**)	—
5e	$CH(CO_2Me)_2$	H	0.29	—[b]	4:1 (50)	24	71	—	45 (**1a**)

[a] Determined by ^{1}H NMR spectroscopy of the crude product. [b] In the absence of potassium propionate (**2b**). [c] Not determined.

Likewise *N*-phthaloyl-β-alanine (**6**) and potassium propionate (**2b**) gave a mixture of the *intramolecular* cyclization/ring-expansion product (**7**) and the β-decarboxylation/alkylation product (**3p**) in isolated yields of 28% and 43%, respectively (Scheme 5). Since solely the potassium salt of **6** is known to undergo decarboxylation upon irradiation in aqueous acetone,[8,14] rapid K/H-exchange obviously precedes

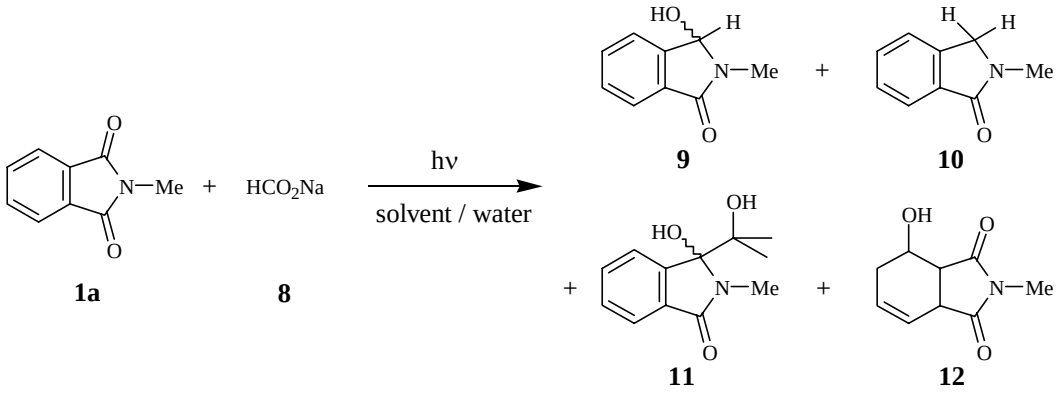
product formation. Compound (**3p**) is formed *via* photoinduced alkylation of the *simple* β-decarboxylation intermediate of **6**.



6 **2b** **3p** (43%) **7** (28%)

Scheme 5

A special case was the irradiation of **1a** in the presence of sodium formate (**8**). Although we have previously reported the formation of the corresponding hydroxyphthalimidine (**9**) in 62% yield,[9] 2-methyl-2,3-dihydroisoindol-1-one (**10**) was formed instead when the original experiment was repeated. During consequent reexamination of this reaction, we noticed that the outcome of the photolysis was, however, sensitive to the reaction conditions applied (Scheme 6; Table 3). Irradiations in aqueous acetone mainly gave the reduction product (**10**) in amounts of 75-85%. Besides, smaller amounts of the hydroxyphthalimidine (**9**; up to 8%) and the diol (**11**; 5-25%) were identified, the latter generated *via* trapping of the solvent acetone. In contrast, when the experiments were undertaken in aqueous acetonitrile, 3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (**9**) became the dominant product (62-67%), and next to **10** (5-18%) the C=C reduction product (**12**) was obtained in amounts of 20-27%. The assumed structure of **12** was supported by NMR and MS spectroscopic analysis, although the mechanism of its formation remains unclear at present.



1a **8** **9** **10** **11** **12**

Scheme 6

The solvent dependence of the *chemoselectivity* was striking, but when the primary photoreduction product (**9**) was finally irradiated in aqueous acetone and in the presence of **8** it was readily converted into 2-methyl-2,3-dihydroisoindol-1-one (**10**). Hence, irradiation of **1a** in the presence of formate is dominated

by stepwise *photoreduction* and *photo-dearomatization*, and both pathways have been described in the photochemistry of phthalimides.[7b,15] In addition, similar phenomena have been reported by Kubo and coworkers for irradiations of other imide chromophores in the presence of secondary amines.[16]

Table 3 Experimental details and product composition of photoreactions involving **8**.

Substrates		Conditions			Product quantity and composition[a]				
1a amount [g]	**8** amount [g]	solvent	solvent/ H_2O [mL]	time [h]	amount [mg]	**9** [%]	**10** [%]	**11** [%]	**12** [%]
0.33	0.79	acetone	4:1 (300)	23	219[b]	trace	75	25	—
0.32	1.35	acetone	1:1 (300)	20	253[b]	8	87	5	—
0.32	0.68	MeCN	1:1 (200)	22	95[c]	67	6	—	27
0.32	1.35	MeCN	1:1 (300)	20	125	62	18	—	20

[a] Determined by ^{1}H NMR analysis of the crude product (± 5%). [b] Significant amounts of 4-hydroxy-4-methyl-2-pentanone (**13**) and of polymeric byproducts. [c] Conversion *ca.* 85%.

As a conclusion the photoinduced decarboxylative addition of potassium carboxylates to phthalimides represents a useful methodology for the synthesis of alkylated hydroxyphthalimidines. The mild conditions and the easy availability (commercially or synthetically) of all starting materials make this procedure a versatile alternative to existing thermal reactions and furthermore suitable for *green photochemistry*.[17]

EXPERIMENTAL

Melting points were measured on a Büchi B-535 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 or Bruker AC 300 F spectrometer (300 MHz and 75.5 MHz, respectively) using the solvent residual peak as internal standard. Chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz. MS spectra were recorded on a Finnigan Incos 500 (CI or EI), HRMS on a Finnigan MAT H-SQ 30 (FAB) spectrometer. IR spectra were recorded on a Perkin-Elmer FT-IR-S 1600 FT/IR spectrophotometer, UV/VIS spectra on a Perkin-Elmer Lambda 7 spectrophotometer using acetonitrile (Merck, puriss. p.a.) as solvent. For combustion analysis an Elementar Vario EL was used. A Rayonet© RPR-208 chamber photoreactor (8 × 3000 Å lamps, *ca.* 800 W, $\lambda = 300 \pm 10$ nm), high-pressure mercury lamp (400 W) or Heraeus Nobelight XeCl excimer lamp (3 kW, $\lambda = 308$ nm) and immersion wall reactors ($\lambda > 280$ nm) were used for irradiation experiments. X-Ray structure analysis was performed on an Enraf-Nonius CAD4 diffractometer. TLC was carried out on Merck Kieselgel 60 F_{254}, column chromatography on silica gel (Macherey & Nagel) 230-240 mesh using mixtures of ethyl acetate

(EA) and *n*-hexane (Hex). Solvents and reagents were commercially available and were used without further purification. The phthalimide derivatives were prepared *via* literature procedures: **1a**,[18a] **1b**,[18b] **1c**,[18c] **1d**,[18d,e] **1e**,[18d,e] **5a**,[18d] **5b**,[18f] **5c**,[18g] **5d**[18h] and **5e**,[18h,i] respectively.

General procedure for the photoreactions: The phthalimide (2 mmol) was dissolved in acetone (240 mL). A solution of potassium carboxylate (5 mmol) in water (60 mL) was added, and the mixture was irradiated at 15-20°C in a Pyrex tube while purging with a slow stream of N_2. The progress of the reaction was followed by TLC analysis. The solution was extracted with CH_2Cl_2 (3 × 100 mL), washed with 5% $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated to dryness. The products were obtained after column chromatography or recrystallization. Experimental details are given in Table 1.

2,3-Dimethyl-3-hydroxy-2,3-dihydroisoindol-1-one (3a). After column chromatography (SiO_2, EA/Hex: 2:1). 138 mg (39%) of **3a** as a slightly beige solid. The conversion was determined by ^{1}H NMR spectroscopic analysis of the crude product as 42%; mp: 125-127°C (lit.,[19] 128-130°C). ^{1}H NMR ($CDCl_3$): δ 1.59 (s, 3H, CH_3), 2.72 (s, 3H, NCH_3), 4.07 (br s, 1H, OH), 7.32 (ddd, *J* = 1.6, 6.8, 7.6, 1H, H_{arom}), 7.41 (d, *J* = 7.6, 1H, H_{arom}), 7.51 (ddd, *J* = 1.2, 6.8, 7.6, 1H, H_{arom}), 7.55 (dd, *J* = 1.6, 6.8, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 23.1 (CH_3), 23.3 (NCH_3), 88.2 (COH), 121.6 (CH), 123.0 (CH), 129.2 (CH), 130.2 (Cq), 132.2 (CH), 148.2 (Cq), 166.8 (CON). MS (EI, 70 eV): *m/z* (%) 160 (11), 159 (M^+-H_2O, 100), 131 (17), 130 (91), 116 (13), 103 (17), 90 (15), 76 (17), 54 (18). IR (KBr disc): ν (cm^{-1}) 3410, 2934, 1774, 1680, 1431, 1139, 1082, 764, 696. Anal. Calcd for $C_{10}H_{11}NO_2$: C 67.78, H 6.26, N 7.90. Found: C 67.98, H 6.18, N 7.93.

3-Ethyl-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3b). After recrystallization from toluene/*n*-hexane. 374 mg (88%) of **3b** as colorless crystals; mp: 140-143°C (lit.,[10b] 141-142°C). ^{1}H NMR (acetone-d_6): δ 0.43 (t, *J* = 7.4, 3H, CH_3), 2.07 (qd, *J* = 7.4, 14.3, 1H, CH_2), 2.18 (qd, *J* = 7.4, 14.3, 1H, CH_2), 2.87 (s, 3H, NCH_3), 5.48 (s, 1H, OH), 7.48 (m, 1H, H_{arom}), 7.60 (m, 3H, H_{arom}). ^{13}C NMR (acetone-d_6): δ 7.9 (CH_3), 23.1 (NCH_3), 29.2 (CH_2), 91.5 (COH), 122.6 (CH), 123.0 (CH), 129.7 (CH), 132.6 (CH), 132.8 (Cq), 147.8 (Cq), 167.2 (CON). MS (EI, 70 eV): *m/z* (%) 173 (M^+-H_2O, 97), 162 (100), 158 (37), 144 (30), 130 (29), 117 (30), 76 (27), 50 (15). IR (CsI disc): ν (cm^{-1}) 3285, 1700, 1684, 1431, 1399, 1095. UV/VIS (CH_3CN): λ_{max} (ε) 249.2 (2989), 217.0 (9612) nm. Anal. Calcd for $C_{11}H_{13}NO_2$: C 69.09, H 6.85, N 7.32. Found: C 68.33, H 7.11, N 7.24.

3-Hydroxy-3-isopropyl-2-methyl-2,3-dihydroisoindol-1-one (3c). Run A (Rayonet): after work-up. 308 mg (86%) of **3c**. Run B (Excimer): after recrystallization from acetone. 5.13 g (63%) of **3c** as a colorless solid. The conversion was determined by GC analysis of the crude product as 73%; mp: 145-147°C (lit.,[10b] 148-149°C). ^{1}H NMR (acetone-d_6): δ 0.41 (d, *J* = 6.8, 3H, CH_3), 1.12 (d, *J* = 6.8, 3H, CH_3), 2.35 (sept, *J* = 6.8, 1H, CH), 2.81 (s, 3H, NCH_3), 5.32 (s, 1H, OH), 7.41 (ddd, *J* = 1.5, 6.8, 7.3, 1H,

H_{arom}), 7.47-7.56 (m, 3H, H_{arom}). ^{13}C NMR (acetone-d_6): δ 16.7 (CH_3), 17.4 (CH_3), 23.6 (NCH_3), 34.6 (CH), 93.2 (COH), 123.0 (CH), 124.1 (CH), 129.8 (CH), 132.0 (CH), 133.5 (Cq), 146.6 (Cq), 166.9 (CON). MS (EI, 70 eV): *m/z* (%) 187 (M^+-H_2O, 14), 172 (22), 162 (100), 133 (17), 105 (8), 77 (19), 50 (17). IR (CsI disc): ν (cm^{-1}) 3271, 2977, 1681, 1677, 1481, 1430, 1368, 1097, 772. Anal. Calcd for $C_{12}H_{15}NO_2$: C 70.22, H 7.37, N 6.82. Found: C 69.83, H 7.62, N 6.94.

3-*sec*-Butyl-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3d). After column chromatography (SiO_2, EA/Hex: 1:1). 386 mg (89%) of **3d** as a colorless solid. The diastereoisomes were assigned as reported earlier,[20] and the diastereoisomeric ratio was determined by ^1H NMR spectroscopic analysis of the crude product as 55:45 (*u*-**3d** : *l*-**3d**); R_f (mixture) = 0.29 (EA/Hex: 1:1); mp (mixture): 102-105°C. Main *u*-diastereoisomer (*u*-**3d**). ^1H NMR ($CDCl_3$): δ 0.35 (d, *J* = 6.9, 3H, CH_3), 0.79-1.22 (m, 2H, CH, CH_2), 0.93 (t, *J* = 7.4, 3H, CH_3), 1.94 (m, 1H, CH_2), 2.55 (s, 3H, NCH_3), 4.84 (br s, 1H, OH), 7.28 (m, 1H, H_{arom}), 7.36-7.51 (br m, 3H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 12.6 (CH_3), 12.8 (CH_3), 23.2 (CH_2), 23.8 (NCH_3), 40.9 (CH), 93.0 (COH), 122.6 (CH), 123.1 (CH), 128.9 (CH), 131.3 (Cq), 131.4 (CH), 145.5 (Cq), 167.3 (CO_2). Minor *l*-diastereoisomer (*l*-**3d**). ^1H NMR ($CDCl_3$): δ 0.26 (m, 1H, CH), 0.71 (t, *J* = 7.4, 3H, CH_3), 0.79-1.22 (m, 1H, CH_2), 1.12 (d, *J* = 6.9, 3H, CH_3), 2.10 (m, 1H, CH_2), 2.55 (s, 3H, NCH_3), 4.84 (br s, 1H, OH), 7.28 (m, 1H, H_{arom}), 7.36-7.51 (br m, 3H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 11.7 (CH_3), 13.3 (CH_3), 23.0 (CH_2), 23.4 (NCH_3), 40.4 (CH), 92.8 (COH), 122.7 (CH), 122.9 (CH), 128.9 (CH), 131.4 (CH), 131.7 (Cq), 145.9 (Cq), 167.4 (CO_2). MS (FAB, 70 eV, mixture): *m/z* (%) 202 (M^+-H_2O, 100), 174 (11), 162 (10), 147 (16), 105 (8). IR (CsI disc, mixture): ν (cm^{-1}) 3279, 2964, 1700, 1684, 1675, 1480, 1073, 775, 703. UV/VIS (CH_3CN, mixture): λ_{max} (ε) 247.4 (3141) nm. HRMS (PI-FAB, mixture): Anal. Calcd for $C_{13}H_{17}NO_2$: 220.134. Found: 220.132 ± 0.002.

3-Hydroxy-3-isobutyl-2-methyl-2,3-dihydroisoindol-1-one (3e). After column chromatography (SiO_2, EA/Hex: 1:1). 220 mg (51%) of **3e** as a colorless, waxy solid. The conversion was determined by ^1H NMR spectroscopic analysis of the crude product as 85%; R_f = 0.43 (EA/Hex: 1:1); mp: 79-83°C. ^1H NMR ($CDCl_3$): δ 0.42 (d, *J* = 7.0, 3H, CH_3), 0.74 (d, *J* = 7.0, 3H, CH_3), 1.02 (m, 1H, CH), 2.01 (m, 2H, CH_2), 2.75 (s, 3H, NCH_3), 3.88 (s, 1H, OH), 7.27-7.56 (m, 4H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 22.9 (CH_3), 23.3 (NCH_3), 24.7 (Cq), 43.5 (CH_2), 90.6 (COH), 122.7 (CH), 123.4 (CH), 130.0 (CH), 131.4 (Cq), 132.3 (CH), 147.7 (Cq), 168.5 (CON). IR (CsI disc): ν (cm^{-1}) 3298, 2924, 1673, 1430, 769, 704. HRMS (PI-FAB): Anal. Calcd for $C_{13}H_{17}NO_2$: 220.134. Found: 220.133 ± 0.002.

3-*tert*-Butyl-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3f). Run A (Rayonet): after column chromatography (SiO_2, EA/Hex: 3:1). 247 mg (57%) of **3f** as a colorless solid. Run B (HP mercury lamp): after recrystallization from acetone. 330 mg (76%) of **3f** as a colorless solid. The conversion was determined by ^1H NMR spectroscopic analysis of the crude product as 89%; mp: 167-169°C. ^1H NMR

($CDCl_3$): δ 0.97 (s, 9H, CH_3), 2.80 (s, 3H, NCH_3), 3.74 (s, 1H, OH), 7.35 (ddd, *J* = 1.2, 7.5, 7.5, 1H, H_{arom}), 7.43 (ddd, *J* = 1.2, 7.5, 7.5, 1H, H_{arom}), 7.56 (d, *J* = 7.5, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 26.1 (CH_3), 27.4 (NCH_3), 39.5 (Cq), 94.9 (COH), 122.8 (CH), 123.9 (CH), 129.1 (CH), 130.9 (CH), 132.1 (Cq), 147.3 (Cq), 168.0 (CON). MS (EI, 70 eV): *m/z* (%) 204 (M^+-CH_3, 8), 202 (7), 189 (10), 164 (100), 133 (10), 117 (4), 105 (7), 91 (4), 77 (7), 56 (14). IR (CsI disc): ν (cm^{-1}) 3278, 2967, 1665, 1613, 1427, 1392, 1071, 766, 708. HRMS (PI-FAB): Anal. Calcd for $C_{13}H_{17}NO_2$: 220.134. Found: 220.130 ± 0.004.

3-(2,2-Dimethylpropyl)-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3g). After column chromatography (SiO_2, EA/Hex: 1:1). 252 mg (80%) of **3g** as a yellowish oil; R_f = 0.36 (EA/Hex: 1:1). ^{1}H NMR (acetone-d_6): δ 0.51 (s, 9H, CH_3), 2.13 (s, 2H, CH_2), 2.81 (s, 3H, NCH_3), 5.11 (s, 1H, OH), 7.39 (ddd, *J* = 0.9, 7.3, 7.5, 1H, H_{arom}), 7.49 (ddd, *J* = 0.9, 7.3, 7.5, 1H, H_{arom}), 7.52-7.57 (m, 2H, H_{arom}). ^{13}C NMR (acetone-d_6): δ 24.2 (NCH_3), 30.3 (Cq), 30.7 (CH_3), 47.6 (CH_2), 90.1 (COH), 123.2 (CH), 124.1 (CH), 129.8 (CH), 132.1 (CH), 132.4 (Cq), 149.2 (Cq), 167.3 (CON). MS (EI, 70 eV): *m/z* (%) 218 (M^+-CH_3, 4), 200 (44), 192 (3), 162 (36), 146 (100), 132 (8), 117 (17), 91 (11), 77 (17), 56 (21), 55 (20), 50 (16). IR (film): ν (cm^{-1}) 3361, 2954, 1682, 1434, 1397, 1055, 772, 704. HRMS (PI-FAB): Anal. Calcd for $C_{14}H_{19}NO_2$: 234.149. Found: 234.147 ± 0.002.

3-Benzyl-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3h). After recrystallization from acetone. 485 mg (88%) of **3h** as colorless crystals; mp: 164-168°C (lit.,[10c] 165-168°C). ^{1}H NMR (acetone-d_6): δ 2.97 (s, 3H, NCH_3), 3.23 (d, *J* = 13.8, 1H, CH_2Ph), 3.42 (d, *J* = 13.8, 1H, CH_2Ph), 5.27 (s, 1H, OH), 6.83 (m, 2H, H_{arom}), 6.98 (m, 3H, H_{arom}), 7.28-7.37 (m, 2H, H_{arom}), 7.45 (m, 2H, H_{arom}). ^{13}C NMR (acetone-d_6): δ 23.9 (NCH_3), 43.0 (CH_2Ph), 91.1 (COH), 122.9 (CH), 123.7 (CH), 127.3 (CH), 128.5 (CH), 129.8 (CH), 130.8 (CH), 132.1 (CH), 133.0 (Cq), 136.3 (Cq), 147.9 (Cq), 166.8 (CON). MS (EI, 70 eV): *m/z* (%) 207 (1), 189 (45), 174 (44), 162 (100), 133 (24), 117 (19), 91 (20), 77 (22), 51 (4). IR (CsI disc): ν (cm^{-1}) 3283, 1684, 1428, 1404, 1073, 774, 759, 703, 606. UV/VIS (CH_3CN): λ_{max} (ε) 228.2 (7373), 255.4 (3226) nm. Anal. Calcd for $C_{16}H_{15}NO_2$: C 75.87, H 5.96, N 5.52. Found: C 75.70, H 6.01, N 5.44. Crystal data for **3h**: *M* = 253.29; monoclinic, space-group *P* 2_1/c; *a* = 9.670(1), *b* = 9.315(1), *c* = 14.886(1) Å; *β* = 98.93(1)°; *V* = 1324.6(2) Å^3; *Z* = 4; d_{calc} = 1.27 g/cm^3; unique reflections: 2878; reflections $I > 2\sigma(I)$: 2042; R_1, wR_2: 0.043, 0.104. The crystallographic data has been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-194007.

Irradiation of *N*-methylphthalimide (1a) in the presence of potassium benzoate (2i). After work-up. 301 mg (86%) of reisolated **1a**.

3-Ethyl-3-hydroxy-2-phenyl-2,3-dihydroisoindol-1-one (3j). After recrystallization from acetone. 277 mg (55%) of **3j** as a colorless solid. The conversion was determined by ^{1}H NMR spectroscopic analysis of the crude product as 60%; mp: 160-163°C (lit.,[10b] 159-160°C). ^{1}H NMR ($CDCl_3$): δ 0.37 (t, *J* = 7.5,

3H, CH_3), 1.89 (qd, *J* = 7.5, 14.3, 1H, CH_2), 2.01 (qd, *J* = 7.5, 14.3, 1H, CH_2), 3.99 (s, 1H, OH), 7.15-7.33 (m, 4H, H_{arom}), 7.43-7.51 (m, 5H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 7.7 (CH_3), 28.7 (CH_2), 93.9 (COH), 121.7 (CH), 123.6 (CH), 126.2 (CH), 126.7 (CH), 128.8 (CH), 129.6 (CH), 131.0 (Cq), 132.8 (CH), 135.5 (Cq), 146.0 (Cq), 167.0 (CON). MS (EI, 70 eV): *m/z* (%) 236 (17), 235 (M^+-H_2O, 100), 220 (96), 206 (22), 191 (5), 178 (9), 165 (10), 152 (7), 130 (20), 115 (16), 102 (21), 77 (58), 63 (7), 50 (11). Anal. Calcd for $C_{16}H_{15}NO_2$: C 75.87, H 5.97, N 5.53. Found: C 76.01, H 6.02, N 5.33.

3-Ethyl-3-hydroxy-2-prop-2-ynyl-2,3-dihydroisoindol-1-one (3k). After work-up. 189 mg (0.88 mmol, 88%) of **3k** as a yellowish oil. ^1H NMR ($CDCl_3$): δ 0.52 (t, *J* = 7.4, 3H, CH_3), 1.98-2.33 (m, 3H, CH_2, CH), 4.08 (d, *J* = 2.5, 1H, NCH_2), 7.40 (ddd, *J* = 1.0, 7.4, 7.4, 1H, H_{arom}), 7.47 (d, *J* = 7.4, 1H, H_{arom}), 7.53 (ddd, *J* = 1.0, 7.4, 7.4, 1H, H_{arom}), 7.64 (d, *J* = 7.4, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 8.0 (CH_3), 26.7 (NCH_2), 29.1 (CH_2), 70.6 (≡CH), 78.9 (C≡), 91.9 (COH), 121.7 (CH), 123.3 (CH), 129.4 (CH), 130.9 (Cq), 132.5 (CH), 146.5 (Cq), 166.9 (CON). HRMS (PI-FAB): Anal. Calcd for $C_{13}H_{13}NO_2$: 216.102. Found: 216.104 ± 0.003.

(1-Ethyl-1-hydroxy-3-oxo-1,3-dihydroisoindol-2-yl)acetic acid methyl ester (3l). After recrystallization from acetone. 332 mg (88%) of **3l** as colorless crystals; mp: 108-110°C. ^1H NMR ($CDCl_3$): δ 0.47 (t, *J* = 7.5, 3H, CH_3), 1.92 (qd, *J* = 7.5, 14.6, 1H, CH_2), 2.08 (qd, *J* = 7.5, 14.6, 1H, CH_2), 3.66 (s, 3H, OCH_3), 3.79 (d, *J* = 17.6, 1H, NCH_2), 4.04 (br s, 1H, OH), 4.34 (d, *J* = 17.6, 1H, NCH_2), 7.40 (ddd, *J* = 1.0, 7.5, 7.5, 1H, H_{arom}), 7.44 (dd, *J* = 1.0, 7.5, 1H, H_{arom}), 7.51 (ddd, *J* = 1.0, 7.5, 7.5, 1H, H_{arom}), 7.66 (dd, *J* = 1.0, 7.5, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 7.5 (CH_3), 28.7 (NCH_2), 39.5 (CH_2), 52.4 (OCH_3), 91.3 (COH), 121.8 (CH), 123.3 (CH), 129.4 (CH), 130.6 (Cq), 132.5 (CH), 146.7 (Cq), 167.6 (CON), 170.5 (CO_2). IR (CsI disc): ν (cm^{-1}) 3298, 1739, 1679, 1426, 1268. Anal. Calcd for $C_{13}H_{15}NO_4$: C 62.64, H 6.07, N 5.62. Found: C 62.91, H 6.23, N 5.48. Crystal data for **3l**: *M* = 249.26; triclinic, space-group $P\bar{1}$; *a* = 7.907(1), *b* = 8.245(1), *c* = 10.717(1) Å; α = 113.75(1), β = 95.04(1), γ = 97.01(1)°; *V* = 627.47(12) $Å^3$; *Z* = 2; d_{calc} = 1.319 g/cm^3; unique reflections: 2426; reflections $I > 2\sigma(I)$: 1539; R_1, wR_2: 0.049, 0.114. The crystallographic data has been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-194006.

[2-(1-Ethyl-1-hydroxy-3-oxo-1,3-dihydroisoindol-2-yl)acetylamino]acetic acid methyl ester (3m). After column chromatography (SiO_2, EA/Hex: 3:1). 297 mg (52%) of **3m** as a colorless oil. ^1H NMR ($CDCl_3$): δ 0.48 (t, *J* = 7.5, 3H, CH_3), 2.06 (qd, *J* = 7.5, 14.6, 1H, CH_2), 2.19 (qd, *J* = 7.5, 14.6, 1H, CH_2), 3.65 (s, 3H, OCH_3), 3.84 (d, *J* = 16.3, 1H, NCH_2), 3.89 (dd, *J* = 5.7, 18.1, 1H, CH_2CO_2), 4.05 (dd, *J* = 5.7, 18.1, 1H, CH_2CO_2), 4.45 (d, *J* = 16.3, 1H, NCH_2), 4.97 (br s, 1H, OH), 7.16 (t, *J* = 5.7, 1H, NH), 7.16 (ddd, *J* = 1.1, 7.2, 7.4, 1H, H_{arom}), 7.51 (d, *J* = 7.2, 1H, H_{arom}), 7.57 (dd, *J* = 7.2, 7.4, 1H, H_{arom}), 7.71 (d, *J* = 7.4, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 7.7 (CH_3), 29.1 ($NHCH_2$), 41.2 (CH_2), 42.2 (NCH_2), 52.4

(OCH_3), 91.8 (COH), 122.0 (CH), 123.4 (CH), 129.5 (CH), 130.4 (Cq), 132.9 (CH), 147.1 (Cq), 168.4 (CON), 170.0 (CONH), 170.5 (CO_2). Anal. Calcd for $C_{15}H_{18}N_2O_5$: C 58.82, H 5.92, N 9.15. Found: C 58.88, H 6.03, N 9.01.

3-Adamant-1-yl-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3n). Run A (Rayonet): a suspension of 322 mg (2.0 mmol) of *N*-methyl phthalimide (**1a**) and 4.37 g (20.0 mmol) of potassium adamantanate (**2j**) in 200 mL of water/acetone (3:97) was irradiated for 106 h. The reaction mixture was evaporated to dryness and the crude product was extracted in a Soxhlet-apparatus with pentane. 1.86 g (69%) of adamantane (**4**) were obtained as a colorless solid. Inspection of the crude product by ^{1}H NMR spectroscopic and TLC analysis showed that most of **1a** remained unchanged. Run B (HP mercury lamp): a clear solution of 320 mg (1.99 mmol) of *N*-methyl phthalimide (**1a**) and 2.18 g (10.0 mmol) of potassium adamantanate (**2j**) in 300 mL of water/acetone (1:1) was irradiated for 3 h. A colorless precipitation occurred which was dissolved in hexane. The reaction mixture was furthermore extracted twice with hexane, the combined hexane layers were dried over $MgSO_4$ and evaporated giving 810 mg (60%) of **4** as a colorless solid. **Adamantane (4).** mp: 211-214°C (lit.,[21] 212-215°C). ^{1}H NMR ($CDCl_3$): δ 1.73 (br s, 12H, CH_2), 1.85 (br s, 4H, CH). ^{13}C NMR ($CDCl_3$): δ 28.3 (CH), 37.8 (CH_2). MS (EI, 70 eV): *m/z* (%) 136 (M^+, 100), 121 (11), 107 (12), 93 (64), 91 (20), 79 (85), 77 (32), 67 (45), 65 (15), 53 (26), 51 (11), 43 (10), 41 (57). IR (KBr disc): ν (cm^{-1}) 2924, 2899, 2846, 1450, 1352, 1101, 798. The acetone/water layer was treated as described in the general procedure. Drying *in vacuo* gave 295 mg of a yellowish solid. ^{1}H NMR spectroscopic and TLC analysis showed that most of the starting material **1a** remained unchanged. Column chromatography (SiO_2, EA/Hex: 1:1) gave 250 mg (78%) of reisolated **1a** and 12 mg (2%) of **3n** as a colorless solid. **3-Adamant-1-yl-3-hydroxy-2-methyl-2,3-dihydroisoindol-1-one (3n).** R_f = 0.48 (EA/Hex: 1:1); mp: 198-205°C. ^{1}H NMR ($CDCl_3$): δ 1.45-1.75 (br m, 9H, CH, CH_2), 1.85-2.00 (m, 6H, CH_2), 2.56 (s, 1H, OH), 3.06 (s, 3H, NCH_3), 7.40-7.50 (m, 2H, H_{arom}), 7.57 (m, 1H, H_{arom}), 7.73 (m, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 28.3 (CH), 28.5 (NCH_3), 36.6 (CH_2), 36.9 (CH_2), 41.5 (Cq), 95.2 (COH), 122.9 (CH), 124.2 (CH), 129.3 (CH), 130.7 (CH), 132.5 (Cq), 146.8 (Cq), 168.2 (CON). HRMS (PI-FAB): Anal. Calcd for $C_{19}H_{24}NO_2$: 298.181. Found: 298.184 ± 0.004. The aqueous layer obtained during work-up was acidified with 2M hydrochloric acid upon which a colorless solid precipitated. Filtration, washing with water and drying in vacuo gave 670 mg (37%) of reisolated 1-adamantanecarboxylic acid.

Irradiation of phthalimides (5a, c-e) in the presence of potassium propionate (2b). Following the above procedure, irradiations of *N*-substituted phthalimides (**5a**, **c-e**) and potassium propionate in water/acetone mixtures gave mixtures of **3b** and *N*-methylphthalimide (**1a**). The product ratios (**3b**:**1a**) were determined by ^{1}H NMR spectroscopic analysis of the crude product. For experimental details and results, see Table 2.

3-Ethyl-3-hydroxy-2-phenylethyl-2,3-dihydroisoindol-1-one (3o). After column chromatography (SiO_2, EA/Hex: 3:1). 316 mg (67%) of **3o** as a colorless solid; mp: 130-133°C. ^{1}H NMR ($CDCl_3$): δ 0.41 (t, *J* = 7.5, 3H, CH_3), 2.00 (qd, *J* = 7.5, 14.4, 1H, CH_2), 2.12 (qd, *J* = 7.5, 14.4, 1H, CH_2), 2.85 (ddd, *J* = 5.3, 10.6, 12.9, 1H, CH_2Ph), 3.01 (ddd, *J* = 5.8, 10.6, 12.9, 1H, CH_2Ph), 3.19 (ddd, *J* = 5.8, 10.6, 13.7, 1H, NCH_2), 3.64 (ddd, *J* = 5.3, 10.6, 13.7, 1H, NCH_2), 3.73 (br s, 1H, OH), 7.13-7.24 (br m, 5H, H_{arom}), 7.29 (ddd, *J* = 1.5, 7.1, 7.5, 1H, H_{arom}), 7.39 (d, *J* = 7.5, 1H, H_{arom}), 7.43 (ddd, *J* = 1.0, 7.1, 7.5, 1H, H_{arom}), 7.50 (d, *J* = 7.5, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 7.7 (CH_3), 29.0 (CH_2), 34.8 (NCH_2), 40.4 (CH_2), 91.9 (COH), 121.6 (CH), 122.9 (CH), 126.3 (CH), 128.4 (CH), 128.8 (CH), 129.3 (CH), 131.3 (Cq), 132.1 (CH), 139.2 (Cq), 146.4 (Cq), 167.6 (CON). MS (FAB, 70 eV): *m/z* (%) 282 (M^{+1}, 79), 264 (48), 220 (50), 185 (75), 161 (100), 147 (40), 105 (58). IR (CsI disc): ν (cm^{-1}) 3265, 1734, 1700, 1684, 1473, 1419, 1091, 760, 699. UV/VIS (CH_3CN): λ_{max} (ε) 250.0 (3928) nm. HRMS (PI-FAB): Anal. Calcd for $C_{18}H_{19}NO_2$: 282.149. Found: 282.153 ± 0.004. ***N*-2-Phenylethylphthalimide (1f).** As second fraction, 107 mg (25%) of **1f** were obtained as a colorless oil. ^{1}H NMR (acetone-d_6): δ 3.36-3.49 (t, *J* = 7.5, 2H, CH_2Ph), 3.85 (t, *J* = 7.5, 2H, NCH_2), 7.20-7.29 (m, 5H, H_{arom}), 7.77 (br s, 4H, H_{arom}). ^{13}C NMR (acetone-d_6): δ 34.9 (CH_2Ph), 39.7 (NCH_2), 123.6 (CH), 127.2 (Cq), 129.1 (CH), 129.5 (CH), 130.9 (Cq), 132.9 (CH), 168.5 (CON). The product ratio was determined by ^{1}H NMR spectroscopic analysis of the crude product as 2.6:1.0 (**3o**:**1f**).

3-Hydroxy-2,3-diethyl-2,3-dihydroisoindol-1-one (3p). Following the above procedure, irradiation of 420 mg (1.92 mmol) of *N*-phthaloyl-β-alanine (**6**) and 1.13 g (10.0 mmol) of potassium propionate in 300 mL of water/acetone (1:4) for 27 h gave, after column chromatography (SiO_2, EA/Hex: 2:1), 168 mg (43%) of **3p** as a colorless oil; R_f = 0.20 (EA/Hex: 2:1). ^{1}H NMR ($CDCl_3$): δ 0.45 (t, *J* = 7.2, 3H, CH_3), 1.18 (t, *J* = 7.2, 3H, CH_3), 2.02 (qd, *J* = 7.2, 14.5, 1H, CH_2), 2.15 (qd, *J* = 7.2, 14.5, 1H, CH_2), 3.13 (qd, *J* = 7.2, 14.5, 1H, NCH_2), 3.43 (qd, *J* = 7.2, 14.5, 1H, NCH_2), 3.80 (br s, 1H, OH), 7.35 (dd, *J* = 7.3, 7.3, 1H, H_{arom}), 7.42-7.52 (m, 3H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 7.8 (CH_3), 14.3 (CH_3), 28.9 (NCH_2), 33.1 (CH_2), 92.1 (COH), 121.5 (CH), 122.9 (CH), 129.3 (CH), 131.5 (Cq), 132.0 (CH), 146.4 (Cq), 167.4 (CON). HRMS (PI-FAB): Anal. Calcd for $C_{12}H_{15}NO_2$: 206.118. Found: 206.120 ± 0.002. **2,3,4,5-Tetrahydro-1*H*-2-benzazepin-1,5-dione (7).** As second fraction, 93 mg (28%) of **7** were obtained as a colorless solid; mp: 163-165°C (lit.,[22] 161-162°C). ^{1}H NMR ($CDCl_3$): δ 2.86 (t, *J* = 6.8, 2H, CH_2CO), 3.43 (m, 2H, CH_2NH), 7.27-7.80 (m, 5H, NH, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 37.2 (CH_2), 46.1 (CH_2NH), 128.5 (CH), 130.2 (CH), 132.0 (CH), 132.1 (Cq), 132.8 (CH), 136.0 (Cq), 171.1 (CONH), 202.1 (CO). Anal. Calcd for $C_{10}H_9NO_2$: C 68.56, H 5.18, N 8.00. Found: C 68.71, H 5.23, N 7.86. The product ratio was determined by ^{1}H NMR spectroscopic analysis of the crude product as 57:43 (**3p**:**7**).

Irradiations of *N*-methylphthalimide (1a) in the presence of sodium formate (8). Following the above procedure, **1a** was irradiated in the presence of **8** in water/acetone or water/acetonitrile mixtures, respectively. The product ratios and compositions were determined by ^{1}H NMR spectroscopic analysis of the crude product. Small amounts of the reaction products were isolated and purified for analysis. For experimental details and results, see Table 3. **3-Hydroxy-2-methyl-2,3-dihydroisoindol-1-one (9).** mp: 127-129°C (lit.,[23] 128-129°C). ^{1}H NMR ($CDCl_3$): δ 2.83 (s, 3H, NCH_3), 4.26 (br d, *J* = 10.3, 1H, OH), 5.53 (d, *J* = 10.3, 1H, CHN), 7.32 (dd, *J* = 7.4, 7.4, 1H, H_{arom}), 7.40 (d, *J* = 7.4, 1H, H_{arom}), 7.47 (dd, *J* = 7.4, 7.4, 1H, H_{arom}), 7.52 (d, *J* = 7.4, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 26.0 (NCH_3), 83.5 (CHN), 122.9 (CH), 123.2 (CH), 129.5 (CH), 131.2 (Cq), 132.1 (CH), 143.8 (Cq), 167.6 (CON). MS (EI, 70 eV): *m/z* (%) 163 (M^+, 72), 162 (100), 146 (60), 133 (37), 105 (57), 91 (19), 77 (49), 50 (29). IR (CsI disc): ν (cm^{-1}) 3287, 1687, 1682, 1673, 1481, 1439, 1056, 750. UV/VIS (CH_3CN): λ_{max} (ε) 246.4 (3227), 227.0 (6550), 218.6 (9285), 207.4 (3495) nm. Anal. Calcd for $C_9H_9NO_2$: C 66.25, H 5.56, N 8.58. Found: C 65.96, H 5.81, N 8.37. **2-Methyl-2,3-dihydroisoindol-1-one (10).** mp: 115-117°C (lit.,[24] 115-116°C). ^{1}H NMR ($CDCl_3$): δ 3.17 (s, 3H, NCH_3), 4.35 (s, 2H, CH_2N), 7.40 (dd, *J* = 1.0, 7.2, 1H, H_{arom}), 7.43 (d, *J* = 7.2, 1H, H_{arom}), 7.50 (dd, *J* = 1.0, 7.2, 1H, H_{arom}), 7.80 (d, *J* = 7.2, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$): δ 29.4 (NCH_3), 51.9 (CH_2N), 122.5 (CH), 123.6 (CH), 128.0 (Cq, CH), 131.1 (CH), 140.9 (Cq), 168.6 (CON). MS (EI, 70 eV): *m/z* (%) 147 (M^+, 100), 128 (10), 118 (75), 91 (32), 77 (15), 51 (10). IR (KBr disc): ν (cm^{-1}) 1672, 1615, 1481, 1445, 1421, 1056, 745. Anal. Calcd for C_9H_9NO: C 73.45, H 6.16, N 9.52. Found: C 73.53, H 6.04, N 9.54. **3-Hydroxy-3-(1-hydroxy-1-methylethyl)-2-methyl-2,3-dihydroisoindol-1-one (11).** R_f = 0.28 (EA/Hex: 2:1); mp: 164-166°C. ^{1}H NMR ($CDCl_3$, 10% DMSO-d_6): δ 0.88 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 2.99 (s, 3H, NCH_3), 3.39 (s, 1H, OH), 5.89 (s, 1H, OH), 7.32 (ddd, *J* = 1.2, 6.8, 7.4, 1H, H_{arom}), 7.38 (ddd, *J* = 1.2, 6.8, 7.4, 1H, H_{arom}), 7.54 (dd, *J* = 1.2, 6.8, 1H, H_{arom}), 7.63 (dd, *J* = 1.0, 6.8, 1H, H_{arom}). ^{13}C NMR ($CDCl_3$, 10% DMSO-d_6): δ 23.7 (NCH_3), 25.9 (CH_3), 26.3 (CH_3), 75.7 (COH), 92.9 (COH), 122.4 (CH), 123.8 (CH), 128.9 (CH), 130.9 (CH), 132.4 (Cq), 146.0 (Cq), 167.6 (CON). MS (EI, 70 eV): *m/z* (%) 204 (M^+-OH, 1), 188 (3), 175 (1), 162 (100), 148 (2), 133 (21), 105 (22), 77 (35), 52 (8). IR (CsI disc): ν (cm^{-1}) 3506, 3226, 1674, 1473, 1426, 1185, 1069, 767. Anal. Calcd for $C_{12}H_{15}NO_3$: C 65.14, H 6.83, N 6.33. Found: C 65.39, H 6.85, N 5.98. **4-Hydroxy-2-methyl-3a,4,5,7a-tetrahydroisoindole-1,3-dione (12).** ^{1}H NMR ($CDCl_3$): δ 2.11 (m, 1H, CH_2), 2.30 (m, 1H, CH_2), 2.86 (s, 3H, NCH_3), 3.10 (dd, *J* = 4.9, 9.0, 1H, CH), 3.37 (m, 1H, CH), 4.18 (ddd, *J* = 4.4, 4.4, 6.7, 1H, CH), 5.76 (m, 1H, =CH), 5.83 (m, 1H, =CH), 8.02 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 24.5 (NCH_3), 30.9 (CH_2), 41.5 (CH), 44.0 (CH), 64.8 (COH), 121.3 (CH), 126.5 (CH), 176.7 (CO), 178.6 (CO). MS (EI, 70 eV): *m/z* (%) 181 (M^+, 15), 163 (14), 153 (8), 124 (8), 112 (10), 97 (10), 96 (100), 95 (52), 81 (21), 78 (15), 77 (14), 67 (21), 66 (18), 56 (8), 54 (8). **4-Hydroxy-4-methyl-2-pentanone (13).** ^{1}H NMR

($CDCl_3$): δ 1.19 (s, 6H, CH_3), 2.12 (s, 3H, $COCH_3$), 2.57 (s, 2H, $COCH_2$), 3.72 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 29.2 (CH_3), 31.7 ($COCH_3$), 53.8 (CH_2), 69.4 (COH), 210.7 (CO).

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