Pergamon

Tetrahedron 58 (2002) 7267–7274

TETRAHEDRON

SET photochemistry of phthalimide anion and its reactivity with hydrogen donors

Cristobal Sánchez-Sánchez, Ezequiel Pérez-Inestrosa, Rafael García-Segura and Rafael Suau*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain

Received 6 May 2002; revised 2 June 2002; accepted 28 June 2002

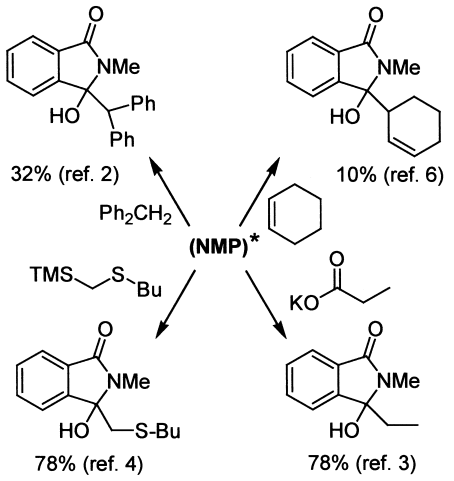
Abstract—The investigation of the photochemistry of phthalimide anion has uncovered its exceptional reactivity with hydrogen donors such as alcohols, toluene, ethers and amines. Photoreactions can be conducted to high conversions and photoadducts are formed in high yield and with predictable regioselectivity. Exploratory studies have revealed that SET from the excited phthalimide anion to phthalimide is a thermodinamically favourable step that produces the electrophilic phthalimidyl radical and is the key step of the process.

1. Introduction

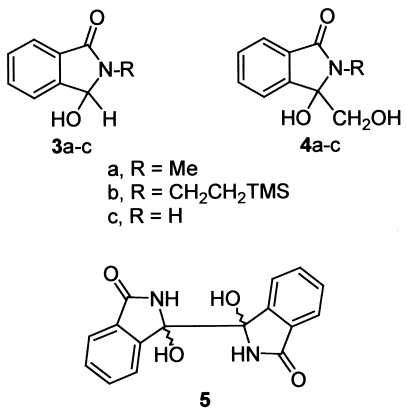
Intra- and intermolecular reactions of phthalimides are widely variable in their photochemical behaviour and possess interesting synthetic applications.[1] The intermolecular photochemistry of phthalimide (PHT-H, **1**) and its *N*-alkyl derivatives in the presence of alkylbenzenes,[2] amines,[2a] carboxylates[3] or silyl derivatives[4] is started in most cases as by a single electron transfer (SET) from the donor to the singlet or triplet excited state of the imide.

For phthalimide and *N*-methylphthalimide (NMP, **2**),[2,5] with a reduction potential around −1.4 V and an excited state energy of approximately 80 kcal/mol (for S_1), the SET is exergonic for electron donors with ionization potentials below 9 eV. Following elimination of a positive charge (a proton for alkylbenzenes and a trimethylsilyl cation for α-silyl-electron donors) or neutral CO_2 (for carboxylates) the radical-ion pairs undergo cross-coupling to form photoaddition products (see Scheme 1 for selected examples). With simple alkenes, concerted [2+2] photocycloaddition with formation of benzazepinediones is the main process unless SET quenches the excited state (in which case allylic photoaddition occurs in non-protic solvents).[6]

Kanaoka's pioneering work[7] showed that irradiation of NMP (**2**) in methanol as hydrogen donor, gives photoreduction and photoaddition products (**3a** and **4a**, respectively) in comparable amounts (20–40%) (Scheme 2). Mariano and Yoon[8] showed that the acetone-sensitised reaction of *N*-2-(trimethylsilyl)ethyl substituted phthalimide in methanol



Scheme 1.



Scheme 2.

Keywords: electron transfer; imides; isoindoles; photochemistry; radicals and radical reactions.

* Corresponding author. Tel.: +34-952-131-934; fax: +34-952-131-941; e-mail: suau@uma.es

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00756-1

also involves reduction (15%) and reductive addition (75%) (**3b** and **4b**). This intermolecular process competes efficiently with intramolecular γ-hydrogen abstraction. Roth[9] found significant differences in the photochemical behaviour of phthalimide. Thus, unsensitized reaction in methanol, ethanol or isopropanol afforded very low yields of the photoreduction product (**3c**, 1–8%); also reductive addition was only observed with better hydrogen donors such as ethanol and isopropanol (21 and 45%, respectively), and **5**, formed by reductive homo-coupling, was the major product in methanol (10%) and in isopropanol (40%).

For some time, our group has been interested in the [2+2]-photocycloaddition of phthalimide to alkenes as a synthetic method for preparing benzazepinediones. In order to prevent quenching by SET, the photochemistry of phthalimide anion (PHT^-) in the presence of alkenes was studied.[10] In early work,[11] we found irradiation of a methanolic solution of sodium phthalimide in the presence of cyclohexene to afford the expected [2]benzazepinedione from the [2+2]-photocycloaddition; however, yields never exceeded 35%. This result was ascribed to competition from the solvent, which gave photoreduction and photoaddition products. Our interest in the role of the solvent in the photoreactivity of phthalimide anion increased upon finding that 2-methyl-2-propanol, a tertiary alcohol scarcely prone taking part in SET or hydrogen abstraction processes, behaves similarly to methanol, the addition product being the main outcome of the photoprocess.

This paper describes the effectiveness of the photochemistry of phthalimide anion in the presence of hydrogen donors such as alcohols, ethers, alkylbenzenes and amines to give reductive-addition products. This photoreaction, which is synthetically valuable, differs in various respects from the photochemistry of phthalimide and its *N*-alkyl derivatives. A mechanism for the reaction, initiated by photoinduced SET from excited phthalimide anion to phthalimide to generate the electrophilic phthalimidyl radical, is proposed.

2. Results and discussion

2.1. Phthalimide anion photochemistry in alcohols

Preparative irradiation (Pyrex) of a methanol solution of phthalimide (13.6 mmol) and NaOH (10 mmol), followed by column chromatography separation, afforded unreacted phthalimide (7%), and hydroxyphthalimidine **3c** (31%), in addition to the photoadduct **4c** (36%) and the oxazolidine **6** (11%) (Scheme 3).

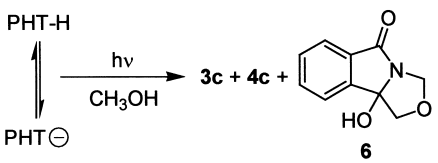
A slower reaction, but similar product distribution, was observed in a methanol solution of sodium phthalimide under identical irradiation conditions. Photoadduct **6** appears to result from thermal reaction of **4c** with formaldehyde, which must be formed by fragmentation of the photochemically produced hydroxymethyl radical.[12] Compound **6** is also produced via a route involving photochemical δ-hydrogen abstraction and cyclization of *N*-methoxymethyl phthalimide.[13]

In order to achieve photocycloaddition with alkenes with no involvement of the solvent, the photoreactivity of phthalimide anion in *tert*-butyl alcohol was investigated. Surprisingly, irradiation of a *t*-BuOH solution of phthalimide anion resulted in the efficient disappearance of the chromophore. Work up of the photolysate resulted in the isolation of a single product **7** (77%).

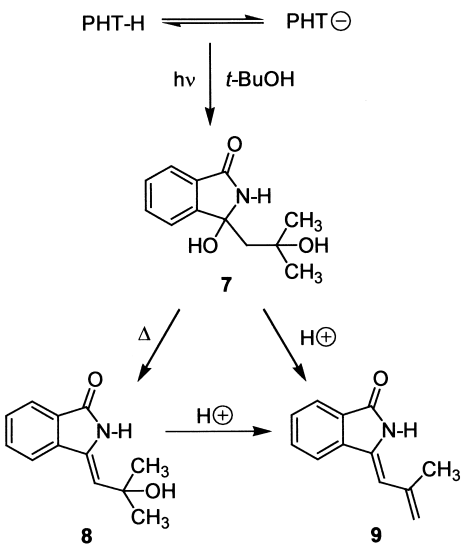
Structure assignment to **7** was made on basis of the ^1H NMR spectrum, which exhibited the signals for the diastereotopic methylene group together with two non-equivalent methyl groups. The attempt at crystallizing of **7** resulted in mono-dehydration to the alkylidene **8**, while the reaction of **7** with TFA/$CHCl_3$ gave the didehydrated diene **9** (Scheme 4). Although *t*-BuOH is considered a poor hydrogen donor, photoaddition of a C–H bond to the electron deficient n,π* carbonyl triplet of benzophenone is known to occur.[14] Moreover, 9,10-anthraquinone also adds *t*-BuOH quite efficiently in an ammonia-catalysed photochemical hydrogen abstraction reaction.[15]

We investigated the photochemistry of 5.4×10^{-2} M *t*-BuOH solutions of phthalimide and *N*-methylphthalimide in parallel with phthalimide anion. The outcome was very clear: after 45 min, no phthalimide remained in the last sample and formation of **7** was almost quantitative; on the other hand, after 90 min, phthalimide and *N*-methyl-phthalimide were recovered unchanged from their respective solutions. With other potential hydrogen donors, such as acetonitrile, however, phthalimide anion was photostable (a 8:1 CH_3CN/H_2O mixture was used to obtain transparent solutions).

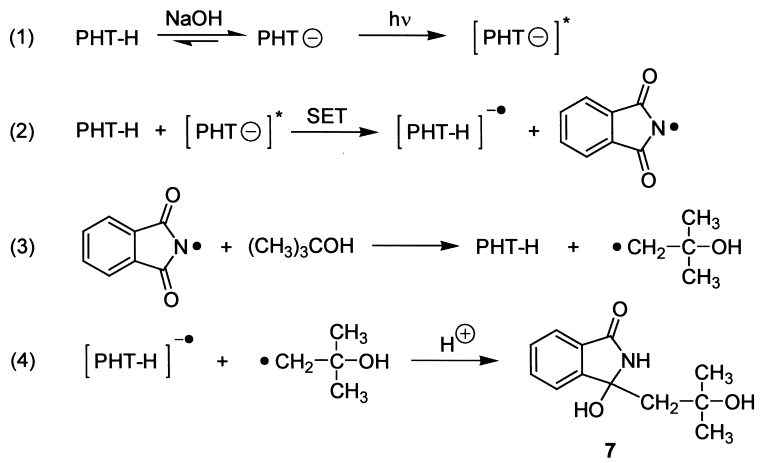
From the above results, we reasoned that a mechanistic pathway in which the excited phthalimide anion, $(PHT^-)^*$,



Scheme 3.



Scheme 4.



Scheme 5.

would capture an H-atom from *t*-BuOH rather than from acetonitrile—with a more favourable bond dissociation energy—was very unlikely. Moreover, $(PHT^{-})^{*}$ was expected to be a rather nucleophilic species that should react more easily with C–H bonds with lower LUMO (CH_3CN) than with C–H bonds with higher HOMO and LUMO[16] (*t*-BuOH), which contradicts the experimental facts.

This results led us to propose a mechanism for the reaction in which phthalimide anion acts as the excited-state electron donor[17] and ground-state phthalimide (PHT-H) as the electron acceptor (Scheme 5).

The absorption spectrum for phthalimide in protic solvents exhibits a weak intensity band ($\varepsilon \approx 1900$) at a long wavelength (295 nm). Upon addition of NaOH the absorption of the conjugate base causes a bathochromic shift and an inflection point at a longer wave-lengths (330 nm) is observed.[18] Thus, irradiation with a Pyrex filter of a 1:1 equivalent mixture of PHT-H/NaOH, results in most of the light being absorbed by the phthalimide anion (Scheme 5, Eq. (1)). Moreover, as the pH of the phthalimide solution is increased, the solution starts to be fluorescent emitting (λ_{exc}=350 nm; λ_{em}=440 nm), maximum emission occurring at a 2:3 phthalimide/NaOH ratio.

We hypothesize that SET from excited phthalimide anion to neutral phthalimide to give phthalimide anion-radical and the electrophilic phthalimidyl radical could take place. It is conceivable that this SET may be governed by the redox properties of donor–acceptor pair and should not be much dependent on the configuration or the multiplicity of the excited state of the donor. The excited state energy for phthalimide anion was estimated to be 3.26 eV from the intercept of the fluorescence and excitation spectra; its oxidation potential is E_{ox} ca. +1.46 V.[19] From these data and a reduction potential for PHT-H of ca. −1.4 V,[2b,5] the Rehm–Weller equation[20] predicts a favourable electron transfer (Scheme 5, Eq. (2)). Phthalimidyl radical is an electrophilic species[21] capable of abstracting hydrogen from the methyl group of the solvent to give the carbon-centred radical (Eq. (3)). Coupling of this radical with the phthalimide anion-radical or its protonated form gives the final photoadduct (Eq. (4)). Importantly, the fluorescence of phthalimide anion is quenched by *N*-methylphthalimide—via the proposed SET mechanism—its reduction potential being quite similar to that of PHT-H.[2b] Also, the rate of disappearance of phthalimide anion on irradiation in *t*-BuOH is strongly dependent on the base concentration; the process is sluggish at low concentration of NaOH but fast at a PHT-H/NaOH ratio close to 1:1 (Fig. 1). Under these conditions, the solution contains enough phthalimide anion to absorb most of the light and sufficient PHT-H to quench the excited state by SET.

2.2. Photochemistry of phthalimide anion with other hydrogen donors

The efficiency of this SET-promoted reaction is expected to be higher with hydrogen donors with lower bond dissociation energies, which are capable stabilizing the carbon-centred radical intermediate. In order to check this assumption, the photochemistry of phthalimide anion with various hydrogen donors was investigated.

Samples to be irradiated were prepared by addition of near

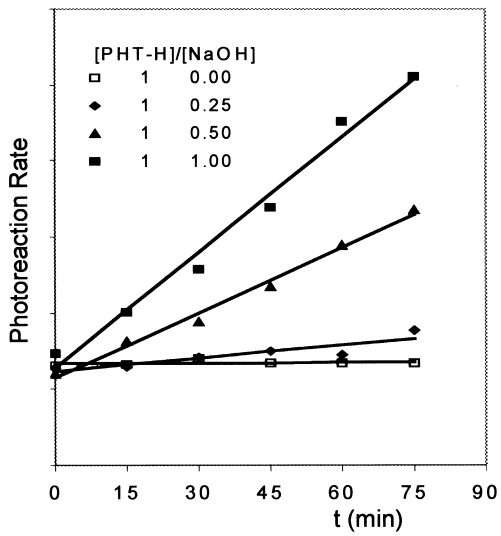
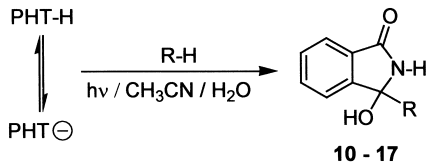


Figure 1. Influence of the NaOH concentration on the photoaddition rate of *t*-BuOH to phthalimide. Aliquots were taken every 15 min and made basic enough to ensure through deprotonation of the remaining PHT-H. ΔO.D. for phthalimide anion were recorded at 320 nm.



Scheme 6.

In the presence of tertiary amines as *N*,*N*-dimethylaniline or triethylamine as hydrogen donors, the photoreactivity of phthalimide anion proceeds as expected and the corresponding photoadducts (**16** and **17**) are formed in good yields. This result differs considerably from that reported for the irradiation of NMP with these amines[2a] (Scheme 7). With *N*,*N*-dimethylaniline, the bis-hydroxyphthalimidine (**18**) is the major product formed, together with the photoadduct **19**.

Table 1. Irradiation of phthalimide anion with various hydrogen-donors

Entry	R–H (mmol)	Irradiation time (h)	Conversion (%)	R	Product	Yield (%)
1	Toluene (93.5)	4	90	$C_6H_5CH_2$	**10**	84
2	Anisole (123)	4	76	$C_6H_5OCH_2$	**11**	70
3	4-Methoxy-toluene (79)	4	92	$(4\text{-}OCH_3)C_6H_4CH_2$	**12**	63
				$(4\text{-}CH_3)C_6H_4OCH_2$	**13**	16
4	*t*-Butyl methyl ether (200)	1	90	$(CH_3)_3COCH_2$	**14**	78
5	Benzyl methyl ether (16)	4	89	$C_6H_5(CH_3O)CH$	**15**	72
6	*N*,*N*-Dimethylaniline (79)	2	85	$C_6H_5(CH_3)NCH_2$	**16**	74
7	Triethylamine (72)	2	90	$(C_2H_5)_2N(CH_3)CH$	**17**	76

Table 2. Irradiation (3 h) of phthalimide and hydrogen donors in the presence and absence of base

Entry	H-Donor	PHT-H/donor (mmol)	NaOH (mmol)	Conversion (%)	Product	Yield (%)
1	Toluene	0.68/13.6	0.68	85	**10**	93
2	Toluene	0.68/13.6	None	<3	–	–
3	TBME	0.68/13.6	0.68	92	**14**	90
4	TBME	0.68/13.6	None	<5	–	–
5	4-Methoxytoluene	0.68/13.6	0.68	86	**12**	79
					13	14
6	4-Methoxytoluene	0.68/13.6	None	<9	–	–

1 equiv. of NaOH to a 4×10^{-2} M solution (7:1 acetonitrile/water) of phthalimide, followed by the hydrogen donor, to obtain a homogeneous solution (Scheme 6 and Table 1).

With toluene, the photoadduct **10** was obtained in 84% yield (at 90% conversion). Based on the proposed mechanism for the reaction, no quenching of the fluorescence of phthalimide anion (λ_{exc}=350 nm; λ_{em}=440 nm) was observed, even at toluene concentrations 60 times higher than that of phthalimide anion. Albini[2b] reported the formation of **10** (28% yield) by irradiation of phthalimide/toluene in acetonitrile (λ=320 nm, 40 h, 36% conversion). The reaction is described to proceed via an electron transfer from toluene to the excited phthalimide, proton elimination from the cation-radical and radical coupling. It is less efficient with NMP, even when toluene is used as solvent.[2a]

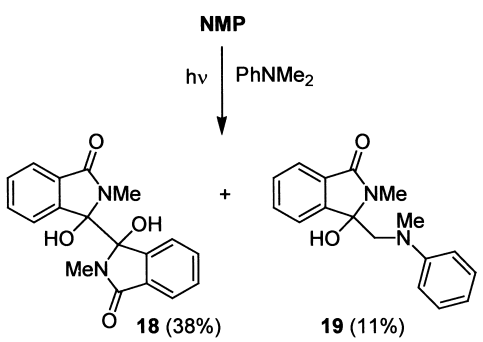
Consistent with the proposed mechanism, irradiation in the presence of anisole afforded the adduct **11** with similar efficiency. With 4-methoxytoluene, competition between H-atom abstraction from both methyl groups was observed, and adducts **12** and **13** isolated. The ratio, close to 5:1, probably reflects the difference in thermodynamic stability between the carbon-centred radical bonded to the aromatic ring or the oxygen atom. With larger C–H bond dissociation energy differences, as in *t*-butyl methyl ether (TBME) or benzyl methyl ether, regioselective capture of hydrogen was observed, and photoadduct **14** and **15**, respectively, was only product obtained. In the absence of base, excitation of phthalimide or NMP resulted in very slow disappearance of the chromophore as measured by HPLC (Table 2).[22]

The proposed reaction mechanism involves SET from the amine to the excited NMF, proton transfer and radical coupling. Nonetheless, over-photoreduction to the 2-methylisoindolinone was the result of the reaction with trietylamine or *N*,*N*-dimethylcyclohexylamine.[2a]

2.3. Dehydration of photoadducts

Photoadducts **10**, **11**, **14**, and **16** were dehydrated to the corresponding alkylidene-isoindanones, **20**–**23**, by reaction with TFA in $CHCl_3$ (Scheme 8).

Under these standard conditions, however, photoadducts **12**, **13**, **15** and **17** gave mixtures of compounds the identification of which was not pursued. With the more sterically hindered photoadducts, only the *Z*-isomer was obtained. The



Scheme 7.

20a, R = Ph
21a, R = OPh
22, R = $OC(CH_3)_3$
23, R = $N(CH_3)Ph$

20b, R = Ph
21b, R = OPh

Scheme 8.

configuration of the double bond was determined from nOe experiments.

3. Conclusions

The above-described results reveal that the photochemistry of phthalimide anion in the presence of hydrogen donors differs considerably from that of NMP or phthalimide and that SET from excited phthalimide anion to ground-state phthalimide is a thermodynamically favourable process that efficiently produces phthalimidyl radical. This species can capture hydrogen from nucleophilic C–H bonds (those with a high bond dissociation energy such as the bonds in *t*-BuOH included) to give the corresponding radicals.

Coupling of phthalimide radical anion with the carbon-centred radical produces the photoadducts in good yields. The electrophilic character of phthalimidyl radical prevents its reaction with other potential hydrogen donors such as acetonitrile. The cumulative results demonstrate that the photochemistry of phthalimide anion in the presence of hydrogen donors differs considerably from that of phthalimide or its *N*-alkyl derivatives. The facts that the photoaddition is a high-yield reaction, can be conducted to high conversion and with predictable regioselectivity, endows this study with synthetic significance.

4. Experimental

Melting points were determined on a Gallenkamp instrument and are given uncorrected. IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer and a Bruker FT-IR Equinox 55 spectrometer equipped with a Specac Golden Gate ATR accesory. Absorption spectra were recorded on an HP 8452A Diode Array Spectrophotometer. Emission spectra were obtained using a JASCO FP-750 Spectrofluorometer interfaced to a Spectra Manager (v 1.30.00) data station. Low-resolution MS (EI and CI) were recorded on a HP-MS 5988A spectrometer operating at 70 eV and high-resolution MS were obtained on a Kratos MS 50 TC mass spectrometer. NMR spectra were recorded on a Bruker WP-200 SY instrument, at 200 MHz for ^1H and 50.3 MHz for ^{13}C. Chemical shifts are given relative to the residual signal for the solvent, δ_H 7.24 ppm and δ_C 77.0 ppm for deuteriochloroform. Coupling constants are given in Hertz. TLC analyses were performed on silica gel 60 F 256 plates and column chromatography was carried out on silica gel 60 (70–230 mesh). Organic solutions were dried with $MgSO_4$. HPLC analyses were carried out on a Hewlett–Packard 1050 chromatograph equipped with an ODS Hypersil column (5 μm, 200×4.6 mm) that was eluted with 40:60 methanol/water (flow 0.8 mL/min) and UV detection at 254 nm. Photochemical reactions were performed at 20°C, using a 250 mL immersion-well photoreactor (Pyrex) equipped with a 125 W medium-pressure mercury lamp (unless otherwise stated). A stream of nitrogen was passed through the solutions during irradiation. Yields are given on consumed phthalimide.

4.1. Irradiation of phthalimide anion in methanol

(i) A stirred solution of phthalimide (2 g, 13.6 mmol), 1 M NaOH (10 mL) in MeOH (160 mL) was irradiated for 60 min. The reaction was monitored by TLC and conversion of phthalimide >90 was achieved. The photolysate was carefully neutralized with 2 M HCl (7 mL) and concentrated to dryness. The solid residue was column chromatographed as above to yield unreacted phthalimide (150 mg, 7%), **3a** (575 mg, 31%), **4a** (801 mg, 36%) and **6** (260 mg, 11%).

(ii) A stirred solution of sodium phthalimide (2.2 g, 13 mmol), in MeOH (160 mL) was irradiated for 90 min. The photolysate was concentrated to dryness and the solid residue was column chromatographed (silica gel, 50% hexane/EtOAc) to give unreacted phthalimide (390 mg, 18%), photoreduced **3c** (375 mg, 23%), photoadduct **4c** (601 mg, 33%), and oxazolidine **6** (211 mg, 11%).

4.1.1. 2,3-Dihydro-3-hydroxy-1*H*-isoindol-1-one (3c). Mp 175–178°C (MeOH) (lit.[23] 179°C).

4.1.2. 2,3-dihydro-3-(hydroxymethyl)-1*H*-isoindol-1-one (4c). White crystals; mp 144–146°C (EtOAc); [Found: C, 60.60; H, 5.07; N, 8.03. $C_9H_9NO_3$ requires C 60.33, H 5.06, N 7.82]; ν_{max} (KBr) cm^{-1} 3188, 1656; δ_H (methanol-d_4) (ppm) 7.7–7.4 (m, 4H, ArH), 3.87 (d, J=11.4 Hz, *H*CH), 3.74 (d, J=11.4 Hz, HC*H*); δ_C (methanol-d_4) (ppm) 171.8 (C1), 149.0 (C3a), 133.7 (C5), 133.17 (C7a), 130.6 (C6),124.0 (C4, C7), 89.1 (C3), 67.0 (CH_2); *m/z* (EI) 177 (M^+, 1), 148 (100), 130 (95). *m/z* (CI, CH_4) 180 [$(M+H)^+$, 100], 162 (59).

4.1.3. 1,9*b*-Dihydro-9*b*-hydroxy-5*H*-oxazolo[4,3-*a*]isoindol-5-one (6). Mp 125–126°C (EtOAc) (lit.[13] 127–128°C (EtOAc/hexane).

4.2. Irradiation of phthalimide/NaOH/2-methyl-2-butanol

A stirred solution of phthalimide (2 g, 13.6 mmol), 1 M NaOH (16 mL) in 2-methyl-2-butanol (150 mL) was irradiated for 5 h. The reaction volume was reduced to 30 mL (at T<40°C), water was added (100 mL) and followed by dilute HCl added to pH 8. Extraction with $CHCl_3$ (3×150 mL) afforded, after drying and concentration, a syrup that solidified on standing (2.3 g, 77%). H NMR for this solid: δ_H ($CDCl_3$ filtered through anhydrous K_2CO_3) (ppm) 7.9 (bs, 1H, NH), 7.7–7.4 (m, 4H, ArH), 5.58 (bs, 1H, OH), 4.19 (s, 1H, OH), 2.45 (d, J=16.5 Hz,

*H*CH), 1.94 (d, *J*=16.5 Hz, HC*H*), 1.28 (s, 3H, CH_3), 1.95 (s, 3H, CH_3) was consistent with the photoadduct **7**. This solid was dissolved in warm acetone and, after addition of hexane, the alkylidene derivative **8** crystallized almost quantitatively.

4.2.1. 3-[(*Z*)-2-Hydroxy-2-methylpropylidene]-1*H*-isoindol-1(2*H*)-one (8). White crystals; mp 126–128°C (acetone); [Found: C, 71.06; H, 6.28; N, 7.02. $C_{12}H_{13}NO_2$ requires C 70.92, H 6.45, N 6.98.]; ν_{max} (KBr) cm^{-1} 3165, 1699; δ_H (acetone-d_6) 9.27 (bs, 1H, NH), 7.78 (d, 1H, *J*=7.3 Hz, H-7), 7.75 (d, 1H, *J*=7.3, 1.4 Hz, H-4), 7.61 (t, 1H, *J*=7.3 Hz, H-5), 7.49 (t, 1H, *J*=7.3 Hz, H-6), 5.77 (s, 1H, H-1′), 3.30 (bs, 1H, OH), 1.47 (s, 6H, 2×CH_3); δ_C (acetone-d_6) 167.6 (C1), 139.3 (C3a), 132.6 (C5), 132.0 (C3), 130.1 (C7a), 129.5 (C6), 123.5 (C7), 120.8 (C4), 114.0 (C1′), 72.8 (C2′), 31.4 (2×CH_3); *m/z* (CI, CH_4) 204 [(M+H)$^+$, 46], 186 (58), 148 (100).

A chloroform (50 mL) solution of photoadduct **7** (250 mg, 1.1 mmol) was treated with TFA (0.5 mL) for 15 min at rt. The reaction product was washed with dilute $NaHCO_3$ and concentrated to obtain diene **9**.

4.2.2. 3-[(*Z*)-2-Methyl-2-propenylidene]-1*H*-isoindol-1(2*H*)-one (9). Syrup, [Found: C, 77.53; H, 6.17; N, 7.77. $C_{12}H_{11}NO_2$ requires C 77.81, H 5.99, N 7.56]; ν_{max} (neat) cm^{-1} 3211, 1678; δ_H (acetone-d_6) 9.21 (bs, 1H, NH), 7.90 (d, 1H, *J*=7.5 Hz, H-7), 7.75 (bd, 1H, *J*=7.5 Hz, H-4), 7.65 (t, 1H, *J*=7.5 Hz, H-6), 7.53 (t, 1H, *J*=7.5 Hz, H-5), 6.33 (d, 1H, *J*=0.8 Hz, H-1′), 5.26 (m, 1H, H-3′), 5.16 (q, 1H, *J*=3, 1.6 Hz, H-3′), 2.20 (q, 1H, *J*=1.6, 0.8 Hz, CH_3); δ_C (acetone-d_6) 168.8 (C1), 140.8 (C3a), 139.8 (C2′), 135.0 (C3), 133.7 (C7a), 132.9 (C5), 129.8 (C6), 123.7 (C7), 120.9 (C4), 118.5 (C3′), 108.5 (C1′), 22.6 (CH_3); *m/z* (EI): 185 (M$^+$, 51), 184 (55), 155 (81), 156 (100).

Three solutions containing: sample A: phthalimide (400 mg), 2-methyl-2-butanol (50 mL) and 1 M NaOH (2.5 mL); sample B: phthalimide (400 mg), 2-methyl-2-butanol (50 mL); sample C: *N*-methylphthalimide (400 mg), 2-methyl-2-butanol) 50 mL), were degassed and externally irradiated. After 45 min, no phthalimide was detected in sample A and no change was observed in samples B and C. The latter two samples were irradiated for a further 45 min, the solvent removed under vacuum and found to contain the unchanged phthalimides.

4.3. General procedure for studying the photochemistry of phthalimide anion with other hydrogen donors

To a solution of phthalimide (1 g, 6.8 mmol) in 140 mL of acetonitrile, 20 mL of H_2O and 5 mL of 1 M NaOH, the amount of hydrogen donor need to obtain a clear, homogeneous mixture was added. The solutions were degassed (N_2) for 30 min and irradiated for the time required to achieve conversions near 90%. The photolysate was neutralized with 1 M HCl and the solvent evaporated in vacuo to give a residue that was subjected to column chromatography (silica gel, 1:1 hexane/EtAcO).

4.3.1. With toluene. (10 mL, 93.5 mmol; 4 h). Unreacted phthalimide (99 mg) and photoadduct **10** (1.2 g, 84%).

*2,3-Dihydro-3-hydroxy-3-(phenylmethyl)-1H-isoindol-1-one (**10**).* White crystals; mp 167–168°C ($CHCl_3$) [lit.[24] 160–161°C]; [Found: C, 75.01; H, 5.49; N, 5.82. $C_{15}H_{13}NO_2$ requires C 75.30, H 5.48, N, 5.85]; ν_{max} (KBr) cm^{-1} 3213, 3070, 1675; δ_H ($CDCl_3$) 7.30 (m, 4H, ArH), 7.28–7.00 (m, 5H, ArH), 6.65 (bs, 1H, NH), 3.80 (s, 1H, OH), 3.35 (d, 1H, *J*=13.5 Hz, H-1′), 3.10 (d, 1H, *J*=13.5 Hz, H-1′); δ_C ($CDCl_3$) 169.4 (C1), 148.2 (C3a), 134.8 (C2′), 132.3, 129.2, 126.7, 123.0, 122.2 (C4, C5, C6, C7, C5′), 130.5 (C7a), 130.3, 127.7 (C3′, C4′, C6′, C7′), 87.6 (C3), 44.8 (C1′); *m/z* (CI, CH_4) 240 [(M+H)$^+$, 100], 222 (42).

4.3.2. With anisole. (15 mL, 123 mmol, 4 h). Unreacted phthlalimide (265 mg) and photoadduct **11** (0.9 g, 70%).

*2,3-Dihydro-3-hydroxy-3-(phenoxymethyl)-1H-isoindol-1-one (**11**).* White crystals; mp 168–169°C (EtOAc/hexane); [Found: C, 70.63; H, 5.19; N, 5.99. $C_{15}H_{13}NO_3$ requires 70.58, H 5.13, N 5.94]; ν_{max} (KBr) cm^{-1} 3376, 3210, 1706; δ_H ($CDCl_3$) 7.85–6.90 (m, 9H, ArH), 6.70 (s, 1H, NH), 4.40 (d, 1H, *J*=9.3 Hz, H-1′), 4.14 (d, 1H, *J*=9.3 Hz, H-1′), 3.55 (s, 1H, OH); δ_C ($CDCl_3$) 169.8 (C1), 157.9 (C2′), 146.3 (C3a), 132.3, 129.4, 122.8, 122.4, 121.0 (C4, C5, C6, C7, C5′), 130.8 (C7a), 128.9 (C4′, C6′), 114.2 (C3′, C7′), 85.8 (C3), 71.3 (C1′); *m/z* (EI) 237 (M$^+$−18, 3), 148 (60), 130 (61), 108 (49), 83 (100); *m/z* (CI, CH_4) 256 [(M+H)$^+$, 100], 238 (47).

4.3.3. With 4-methoxytoluene. (10 mL, 79 mmol, 4 h). Unreacted phthalimide (92 mg) and photoadducts **12** (1.05 g, 63%) and **13** (0.26 g, 16%).

*2,3-Dihydro-3-hydroxy-3-[4-methoxypheny)methyl-1H-isoindol-1-one (**12**).* White crystals; mp 142–143°C (EtOAc/hexane); [Found: C, 71.05; H, 5.76; N, 5.22. $C_{16}H_{15}NO_3$ requires C 71.36, H 5.61, N 5.10]; ν_{max} (KBr) cm^{-1} 3416, 3266, 1699; δ_H ($CDCl_3$) 7.60–7.25 (m, 4H, ArH), 7.20 (bs, 1H, NH), 7.00 (d, 2H, *J*=8.5 Hz, H-3′, H-7′), 6.70 (d, 2H, *J*=8.5 Hz, H-4′, H-6′), 4.40 (s, 1H, OH), 3.07 (s, 3H, OCH_3), 3.26 (d, 1H, *J*=13.7 Hz, H-1′), 3.05 (d, 1H, *J*=13.7 Hz, H-1′); δ_C ($CDCl_3$) 169.4 (C1), 158.2 (C5′), 148.2 (C3a), 132.2, 129.0, 122.9, 122.2 (C4, C5, C6, C7), 131.2 (C3′, C7′), 130.5 (C7a), 126.8 (C2′), 113.1 (C4′, C6′), 87.7 (C3), 54.8 (OCH_3), 43.9 (C1′); *m/z* (EI) 251 (M$^+$−18, 27), 236 (14), 148 (46), 130 (58), 122 (100); *m/z* (CI, CH_4) 270 [(M+H)$^+$, 77], 252 (100), 148 (31).

*2,3-Dihydro-3-hydroxy-3-[(4-methylphenoxy)methyl]-1H-isoindol-1-one (**13**).* White crystals; mp 138–139°C (EtOAc/hexane); [Found: C, 70.97; H, 5.70; N, 5.10. $C_{16}H_{15}NO_3$ requires C 71.36, H 5.61, N 5.10]; ν_{max} (neat) cm^{-1} 3296, 1690; δ_H ($CDCl_3$) 7.64–7.41 (m, 4H, ArH), 7.00 (d, 2H, *J*=8.5 Hz, H-3′), H-7′), 6.75 (d, 2H, *J*=8.5 Hz, H-4′, H-6′), 4.69 (s, 1H, OH), 4.27 (d, 1H, *J*=9.4 Hz, H1′), 4.11 (d, 1H, *J*=9.4 Hz, H1′), 2.24 (s, 3H, Me); δ_C ($CDCl_3$) 169.8 (C1), 156.1 (C2′), 146.2 (C3a), 132.5, 129.6, 123.4, 122.6 (C4, C5, C6, C7), 130.9, 130.4 (C7a, C5′), 129.7 (C4′, C6′), 114.6 (C3′, C7′), 86.4 (C3), 71.8 (C1′), 20.2 (CH_3); *m/z* (EI) 269 (M$^+$, 4), 251 (14), 148 (81), 130 (74), 122 (87); *m/z* (CI, CH_4) 270 [(M+H)$^+$, 100], 252 (41).

4.3.4. With *tert*-butyl methyl ether. (25 mL, 200 mmol, 1 h). Unreacted phthalimide (90 mg) and photoadduct **14** (1.15 g, 78%).

*2,3-Dihydro-3-hydroxy-3-[(1,1-dimethylethoxy)methyl]-1H-isoindol-1-one (**14**).* White crystals; mp 132–134°C ($CHCL_3$/hexane); [Found: C, 66.41; H, 7.31; N, 5.94. $C_{13}H_{17}NO_3$ requires C 66.36, H 7.18, N 5.95]; ν_{max} (KBr) cm^{-1} 3228, 1678; δ_H ($CDCl_3$) 7.74 (d, 1H, J=7.2 Hz, H-7), 7.57–7.46 (m, ArH), 6.68 (s, 1H, NH), 3.93 (s, 1H, OH), 3.80 (d, 1H, J=8.6 Hz, H-1′), 3.43 (d, 1H, J=8.6 Hz, H-1′), 1.21 (s, 9H, 3×CH_3); δ_C ($CDCl_3$) 169.2 (C1), 146.1 (C3a), 131.3 (C7a), 132.3, 129.6, 123.5 y 122.6 (C4, C5, C6, C7), 86.4 (C3), 74.1 (C2′), 66.8 (Cl′), 27.3 (CH_3); *m/z* (EI) 217 (M^+-18, 1), 178 (8) 161 (8), 148 (100), 130 (43), 102 (10); *m/z* (CI, CH_4) 236 [$(M+H)^+$, 100], 216 (55).

4.3.5. With benzyl methyl ether. (2 mL, 16.2 mmol, 4 h). Unreacted phthalimide (100 mg) and photoadduct **15** (1.2 g, 72%).

*2,3-Dihydro-3-hydroxy-3-[methoxy(phenyl)methyl]-1H-isoindol-1-one (**15**, mixture of isomers).* White crystals; mp 180–183°C ($CHCl_3$); [Found: C, 71.45; H, 5.70; N, 5.24. $C_{16}H_{15}NO_3$ requires C 71.36, H 5.61, N 5.10]; ν_{max} (neat) cm^{-1} 3348, 3199, 1678; δ_H ($CDCl_3$) 7.75–6.90 (m, 18H, ArH), 6.72 (s, 1H, NH), 6.35 (s, 1H, NH), 4.59 (s, 1H, H-1′), 4.39 (s, 1H, H-1′), 3.98 (s, 1H, OH), 3.61 (s, 1H, OH), 3.40 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3); δ_C ($CDCl_3$) 169.7 (C1), 169.5 (C1), 146.1 (C3a), 145.8, (C3a), 135.3 (C2′), 134.9 (C2′), 131.1 (C7a), 130.8 (C7a), 131.8, 131.7, 129.1, 129.0, 128.2, 127.9, 127.8, 127.7, 127.2, 123.5, 122.8, 122.6, 122.4 (C4, C5, C6, C7, C3′, C7′), 88.4 (C3), 88.3 (C3), 86.9 (C1′), 86.8 (C1′), 56.9 (OCH_3), 56.7 (OCH_3); *m/z* (EI) 251 (M^+-18, 2), 148 (49) 130 (60), 121 (100); *m/z* (CI, CH_4) 270 [$(M+H)^+$, 100], 252 (43).

4.3.6. With *N*,*N*-dimethylaniline. (10 mL, 78.5 mmol, 2 h). Unreacted phthalimide (150 mg) and photoadduct **16** (1.1 g, 74%).

*2,3-Dihydro-3-hydroxy-3-{[methyl(phenyl)amino]methyl}-1H-isoindol-1-one (**16**).* White crystals; mp 155–156°C (EtOAc); [Found: C, 71.70; H, 6.11; N, 10.36. $C_{16}H_{16}N_2O_2$ requires C 71.62, H 6.01, N 10.44]; ν_{max} (KBr) cm^{-1} 3211, 1689; δ_H ($CDCl_3$) 7.60–6.60 (m, 9H, ArH), 7.05 (s, 1H, NH), 4.10 (s, 1H, OH), 3.84 (d, 1H, J=15.2 Hz, H-1′), 3.57 (d, 1H, J=15.2 Hz, H-1′), 3.00 (s, 3H, NCH_3); δ_C ($CDCl_3$) 169.3 (C1), 149.7 (C2′), 147.4 (C3a) 132.4, 129.4, 123.1, 122.6, 116.8 (C4, C5, C6, C7, C5′), 128.6 (C4′, C6′), 112.4 (C3′, C7′), 130.6 (C7a), 88.4 (C3), 60.0 (C1′), 39.7 (CH_3); *m/z* (EI) 268 (M^+, 3), 151 (19), 130 (17), 120 (100); *m/z* (CI, CH_4) 269 [$(M+H)^+$, 100], 251 (39).

4.3.7. With triethylamine. (10 mL, 72.3 mmol, 2 h). Unreacted phthalimide (101 mg) and photoadduct **17** (1.18 g, 76%).

*[1-(Diethylamino)ethyl]-2,3-dihydro-3-hydroxy-1H-isoindol-1-one (**17**).* White crystals; mp 172–174°C (EtOAc); [Found: C, 67.75; H, 8.00; N, 11.14. $C_{14}H_{20}N_2O_2$ requires C 67.72, H 8.12, N 11.2]; ν_{max} (neat) cm^{-1} 3189, 1693; δ_H ($CDCl_3$) 7.79–7.40 (m, 4H, ArH), 6.65 (bs, 1H, NH), 6.33 (bs, 1H, OH), 3.30 (q, 1H, J=6.9 Hz, H-1′), 2.61 (m, 4H, H-3′, H-4′), 1.17 (t, 6H, J=7.1 Hz, H-5′, H-6′), 0.76 (d, 3H, J=6.9 Hz, H2′); δ_C ($CDCl_3$) 170.4 (C1), 148.0 (C3a), 132.4, 129.3, 123.2, 121.6, (C4, C5, C6, C7), 132.1 (C7a), 87.5 (C3), 61.9 (C1′), 44.6 (C3′, C4′), 13.8 (C5′, C6′), 7.5 (C2′); *m/z* (EI) 230 (M^+-18, 1), 100 (100); *m/z* (CI, CH_4) 249 [$(M+H)^+$, 100], 231 (17).

4.3.8. General procedure for the dehydration of photoadducts 10, 11, 14 and 16. A chloroform solution (50 mL) of photoadduct (0.8 mmol) and TFA (0.1 mL, 1.3 mmol) was stirred at 25°C for 4 h. The resulting solution was washed with saturated aqueous Na_2CO_3 and the organic solution dried and concentrated in vacuo. When a single isomer was formed, the residue was crystallized from EtOH, EtOAc or EtOAc/hexane mixtures. When both isomers were formed, the residue was subjected to silicagel column chromatography (2:1 hexane/EtOAc).

*3-[(Z)-Phenylmethylidene]-1H-isoindol-1(2H)-one (**20a**).* White crystals; mp 181–182°C (EtOH); [Found: C, 81.99; H, 4.88; N, 6.27. $C_{15}H_{11}NO$ requires C 81.53, H 5.01, N 6.33]; ν_{max} (KBr) cm^{-1} 3255, 1705; δ_H ($CDCl_3$) 8.46 (bs, 1H, NH), 7.87 (d, 1H, J=7.3 Hz, H-7), 7.79 (d, 1H, J=7.8 Hz, H-4), 7.63 (dt, 1H, J=7.8, 1.0 Hz, H-5), 7.55–7.26 (m, 6H, ArH), 6.55 (s, 1H, H-1′); δ_C ($CDCl_3$) 169.6 (C1), 138.1, 134.6 and 132.6 (C7a, C3a, C3, C2′), 132.1, 128.8, 128.4, 127.4, 123.2, 119.6 (C4, C5, C6, C7, C3′, C7′), 106.4 (C1′); *m/z* (EI) 221 (M^+, 100), 193 (21), 165 (19).

*3-[(E)-Phenylmethylidene]-1H-isoindol-1(2H)-one (**20b**).* White crystals; mp 172–173°C (EtOH); [Found: C, 81.81; H, 5.14; N, 6.30. $C_{15}H_{11}NO$ requires C 81.53, H 5.01, N 6.33]; ν_{max} (KBr) cm^{-1} 3156, 1699; δ_H ($CDCl_3$) 9.59 (s, 1H, NH), 7.89 (d, 1H, J=7.2 Hz, H-7), 7.53–7.33 (m, 8H, ArH), 6.73 (s, 1H, H-1′); δ_C ($CDCl_3$) 168.9 (C1), 135.5, 135.0, 134.7, 131.5 (C7a, C3a, C2′, C3), 131.7, 129.4, 129.1, 128.6, 127.6, 123.3 (C4, C5, C6, C7, C3′, 4′, C6′, C7′), 112.6 (C1′); *m/z* (EI) 221 (M^+, 100), 193 (24), 165 (21).

*3-[(Z)-Phenoxymethylidene]-1H-isoindol-1(2H)-one (**21a**).* White crystals; mp 168–170°C (EtOAc/hexane); [Found: C, 75.86; H, 4.76; N, 5.85. $C_{15}H_{11}NO_2$ requires C 75.94, H 4.67, N 5.90]; ν_{max} (neat) cm^{-1} 3184, 1675; δ_H ($CDCl_3$) 8.25 (s, 1H, NH), 7.90 (d, 1H, J=7.3 Hz, H-7), 7.60–7.10 (m, 8H, ArH), 6.96 (s, 1H, H-1′); δ_C ($CDCl_3$) 167.0 (C1), 156.8 (C2′), 136.1 (C3a), 131.8, 129.8, 128.1, 124.0, 123.8, 123.6, 118.7, 116.5 (C4, C5, C6, C7, C3′, 4′, C6′, C7′, C1′), 129.0 (C7a), 121.5 (C3); *m/z* (EI) 237 (M^+, 100), 180 (13), 160 (35), 132 (43).

*3-[(E)-Phenoxymethylidene]-1H-isoindol-1(2H)-one (**21b**).* White crystals; mp 145–146°C (EtOAc/hexane); [Found: C, 76.22; H, 4.79; N, 5.74. $C_{15}H_{11}NO_2$ requires C 75.94, H 4.67, N 5.90]; ν_{max} (KBr) cm^{-1} 3040, 1703; δ_H ($CDCl_3$) 9.25 (s, 1H, NH), 8.12 (d, 1H, J=7.6 Hz, H-7), 7.90 (d, 1H, J=7.6 Hz, H-4), 7.63 (dt, 1H, J=7.6, 1.1 Hz, H6), 7.50 (dt, 1H, J=7.6, 1.1 Hz, H-5), 7.44–7.13 (m, 5H, ArH), 7.10 (s, 1H, H-1′); δ_C ($CDCl_3$) 168.5 (C1), 157.1 (C2′), 135.0 (C3a), 132.3, 129.9, 129.1, 128.7, 124.4, 123.7, 123.3, 116.4 5 (C4, C5, C6, C7, C3′, 4′, C6′, C7′, C1′) 129.7 (C7a), 123.9 (C3); *m/z* (EI) 237 (M^+, 100), 180 (12), 160 (30), 132 (35).

*3-[(Z)-(1,1-Dimethylethoxy)methylidene]-1H-isoindol-1(2H)-one (**22**).* White crystals; mp 130–132°C (EtOAc/hexane); [Found: C, 71.79; H, 6.99; N, 6.41. $C_{13}H_{15}NO_2$ requires C 71.87, H 6.96, N 6.45]; ν_{max} (KBr) cm^{-1} 3256, 1671; δ_H ($CDCl_3$) 7.84 (d, 1H, J=7.5 Hz, H7), 7.67 (bs, 1H, NH), 7.51–7.31 (m, 3H, ArH), 6.71 (s, 1H, H-1′), 1.39 (s, 9H, 3×CH_3); δ_C ($CDCl_3$) 166.9 (C1), 136.5 (C5a), 128.6 (C7a), 131.2, 126.7, 126.7, 123.5, 123.4 (C4, C5, C6, C7), 118.0 (C1′), 118.6 (C3), 78.8 (C2′), 27.9 (3×CH_3); *m/z* (EI) 217 (M^+, 8), 161 (100), 133 (28), 104 (24).

3-{(Z)-[Methyl(phenyl)amino]methylidene}-1H-isoindol-1(2H)-one (23). White crystals; mp 203–204°C (EtOAc); [Found: C, 76.82; H, 5.71; N, 11.24. $C_{16}H_{14}N_2O$ requires C 76.78, H 5.64, N 11.19]; ν_{max} (neat) cm^{-1} 3260, 1677; δ_H ($CDCl_3$) 8.11 (bs, 1H, NH), 7.82 (d, 1H, J=7.8 Hz, H-7), 7.62–6.98 (m, 8H, ArH), 6.51 (s, 1H, H-1′), 3.49 (s, 3H, NCH_3); δ_C ($CDCl_3$) 167.5 (C1), 145.9 (C2′), 138.3 (C3a), 131.5, 126.4, 123.4, 122.2 (C4, C5, C6, C7), 129.4, 118.0 (C3′, C7′, C4′, C6′), 117.7 (C5′), 129.1 (C7a), 116.5 (C3), 40.0 (CH_3); *m/z* (EI) 250 (M^+, 53), 244 (14), 145 (10), 132 (16), 91 (100).

Acknowledgments

The authors wish to acknowledge financial support from Spain's DGES (project PB97-1077) and DGI (project BQU2001-1890).

References

1. (a) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407–413. (b) Mazzocchi, P. H. *Organic Photochemistry*, Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, pp 421–471 Chapter 5. (c) Coyle, J. D. In *Synthetic Organic Photochemistry*. Horspool, W. M., Ed.; Plenum: New York, 1984; pp 259–283 Chapter 4. (d) Mauder, H.; Griesbeck, A. G. In *CRC Handbook of Organic Photochemistry and Photobiology*. Horspool, W. M., Song, P.-S., Eds.; CRC: Boca Raton, FL, 1995; pp 513–521 Chapter 42. (e) Griesbeck, A. G. *Chimia* **1998**, *52*, 272–283. (f) Griesbeck, A. G.; Kramer, W.; Oelgemöller, M. *Synlett* **1999**, 1169–1178. (g) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **2001**, *34*, 523–533.
2. (a) Kanaoka, Y.; Sakai, K.; Murata, R.; Hatanaka, Y. *Heterocycles* **1975**, *3*, 719–722. (b) Frecero, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1993**, *58*, 1740–1745.
3. (a) Griesbeck, A. G.; Oelgemöller, M. *Synlett* **1999**, 492–494. (b) Griesbeck, A. G.; Oelgemöller, M. *Synlett* **2000**, 71–72. (c) Griesbeck, A. G.; Oelgemöller, M.; Lex, J. *Synlett* **2000**, 1455–1457. (d) Griesbeck, A. G.; Oelgemöller, M.; Lex, J.; Haeuseler, A.; Schmittel, M. *Eur. J. Org. Chem.* **2001**, 1831–1833.
4. Yoon, U. C.; Kim, J. U.; Mariano, P. S. *Heterocycles* **1989**, *29*, 1041–1063.
5. Coyle, J. D.; Newport, G. L.; Harriman, A. *J. Chem. Soc., Perkin Trans.* **1978**, 133–137.
6. (a) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *Tetrahedron Lett.* **1978**, *19*, 4361–4364. (b) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, 851–854. (c) Hayashi, H.; Nagakura, S.; Kubo, Y.; Maruyama, K. *Chem. Phys. Lett.* **1980**, *72*, 291–294. (d) Mazzocchi, P. H.; Klingler, L. *J. Am. Chem. Soc.* **1984**, *106*, 7567–7572. (e) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1985**, *50*, 1426–1435. (f) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *J. Org. Chem.* **1985**, *50*, 2681–2684.
7. (a) Kanaoka, Y.; Koyama, K. *Tetrahedron Lett.* **1972**, *13*, 4517–4520. (b) Kanaoka, Y.; Sato, E. *Chem. Pharm. Bull.* **1978**, *26*, 989–992.
8. Lee, Y. J.; Ling, R.; Mariano, P. S.; Yoon, U. C.; Kim, D. U.; Oh, S. W. *J. Org. Chem.* **1996**, *61*, 3304–3314.
9. Roth, H. J.; Hundeshagen, G. *Arch. Pharmaz.* **1976**, *309*, 58–62.
10. Suau, R.; García-Segura, R.; Sánchez-Sanchez, C.; Pérez-Inestrosa, E. *Eur. J. Org. Chem.* **2002**, 1903–1911.
11. Suau, R.; García-Segura, R. *Tetrahedron Lett.* **1988**, *29*, 1071–1074.
12. Oxazolidines are also formed in the addition of hydromethyl radical (photochemically generated from benzophenone/MeOH) to ketoximes: Torrente, S.; Alonso, R. *Org. Lett.* **2001**, *3*, 1985–1987.
13. Sato, Y.; Nakai, H.; Wada, M.; Ogiwara, H.; Mizoguchi, T.; Migita, Y.; Hatanaka, Y.; Kanaoka, Y. *Chem. Pharm. Bull.* **1982**, *30*, 1939–1945.
14. Gramain, J. C.; Remuson, R. *J. Org. Chem.* **1985**, *50*, 1120–1122.
15. Wubbels, G. G.; Monaco, W. J.; Johnson, D. E.; Meredith, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 1036–1037.
16. Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*. Wiley: Chichester, 1995; pp 49–72.
17. Photoinduced electron transfer from phthalimide anion to 1-iodoadamantane has been recently reported: Bajo Maquieira, M.; Peñéñory, A.-B.; Rossi, R. A. *J. Org. Chem.* **2002**, *67*, 1012–1015.
18. Berci-Filho, P.; Quina, F. H.; Gehlen, M. H.; Politi, M. J.; Neumann, M. G.; Barros, T. C. *J. Photochem. Photobiol. A: Chem.* **1995**, *92*, 155–161.
19. The electrochemical oxidation of potassium phthalimide in DMF at 13°C is monoelectronic, fast, irreversible with a lifetime shorter than 2×10^{-4} s. Marquet, J.; Gallardo, I. Universitat Autónoma de Barcelona, Spain, private communication.
20. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.
21. Phthalimidyl radical generated by photolysis of *N*-halophthalimides adds to electron-rich alkenes and alkynes in a chain reaction: (a) Kirsch, A.; Lüning, U. *J. Prak. Chem.-Chem. Ztg.* **1998**, *340*, 129–134. (b) Kirsch, A.; Lüning, U.; Krüger, O. *J. Prak. Chem.-Chem. Ztg.* **1999**, *341*, 649–656. (c) Wille, U.; Krüger, O.; Kirsch, A.; Lüning, U. *Eur. J. Org. Chem.* **1999**, 3185–3189.
22. The photoaddition of THF to NMP has been reported. (a) Kanaoka, Y.; Hatanaka, Y. *Chem. Pharm. Bull.* **1974**, *22*, 2205–2206. (b) Roth, H. J.; Schwarz, D. *Arch. Pharmaz.* **1975**, *309*, 52–58.
23. Horii, Z-I.; Tamura, Y. *J. Org. Chem.* **1961**, *26*, 2273–2276.
24. Marsini, A.; Scartoni, V. *Gazz. Chim. Ital.* **1972**, *102*, 507–516.