CROATICA CHEMICA ACTA
CCACAA, ISSN 0011-1643, e-ISSN 1334-417X
Croat. Chem. Acta **83** (2) (2010) 179–188.
CCA-3408

Original Scientific Article

Photochemistry of *N*-alkyl and *N*-aryl Substituted Phthalimides: H-Abstractions, Single Elelctron Transfer and Cycloadditions*

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RECEIVED MARCH 10, 2009; REVISED NOVEMBER 16, 2009; ACCEPTED NOVEMBER 18, 2009

Abstract. The phthalimide chromophore shows a broad spectrum of intra- and intermolecular photochemical transformations. Photoreactions of phthalimide derivatives can be classified in three main groups: H-abstraction, cycloaddition and single electron transfer. The photoproducts are aza-heterocycles, useful synthons in the synthesis of more complex heterocyclic and natural products. The aim of this review is to provide an overview of the synthetic applicability of these processes, as well as to point out the parameters that influence the photochemical reactivity of phthalimides.

Keywords: phthalimides, photochemistry, H-abstractions, photoinduced electron transfer, cycloadditions

INTRODUCTION

The carbonyl group is probably the most investigated chromophore,[1–3] and consequently, its photochemistry has been intensively studied since the pioneering work of Ciamician,[4] and Paterno.[5] In the scope of that research, already in 1970s, Kanaoka brought the phthalimide derivatives into focus and published the first investigations of the photochemical reactivity of that chromophore.[6] However, phthalimides are still a subject of widespread interest.[7–17] The principal reasons for this are their interesting photophysics, which is still not completely understood,[18–27] and their applications in organic synthesis.[28–35]

Phthalimides are aromatic imide derivatives characterized by the presence of an absorption band with a maximum at 290−300 nm ($\varepsilon \approx 1-2 \times 10^3$ mol^{-1} dm^3 cm^{-1}), corresponding to a π,π* transition. In addition, there is a close-lying n,π* transition which is overlapped by the π,π* absorption band and seen as a shoulder only in nonpolar solvents.[6,18] *N*-alkylphthalimides are weakly fluorescent.[18,21,22] The major deactivation channel of the excited singlet state of most *N*-alkylphthalimides is intersystem crossing, resulting in population of triplet states.[17,23,24] Therefore, singlet state lifetimes are generally very short, (*e.g.* for *N*-methylphthalimide in CH_3CN τ_F = 0.2 ns)[23] and quantum yields of intersystem crossing are high, Φ_{ISC} = 0.5−1. Triplet lifetimes are longer, generally in the microsecond timescale (τ_T = 1−10 μs).[19,20,23–26] Consequently, the photochemistry of phthalimide derivatives mostly originates from the excited triplet states. The reports on the photophysics of the phthalimide chromophore are controversial, primarily due to a disagreement as to the energy levels of the phthalimide excited states. In polar solvents, the proposed order of excited states is: ^{1}π,π*, ^{1}n,π*, ^{3}n,π*, ^{3}π,π*, with energy levels 395, 334, 298 and 288 kJ mol^{-1},[18] or 384, 368, 343 and 297 kJ mol^{-1},[23] respectively. In alcohols, the proposed order, starting from the state of highest energy, is ^{1}n,π*, ^{3}π,π*,^{1}π,π*, ^{3}n,π*. In the presence of water the triplet states are exchanged.[21,22] However, these data refer to measurements at −196 °C. Since the energy level of n,π* states is very dependant on solvent polarity and proticity, different estimates of energy levels are not surprising. In recent reports by Griesbeck and Görner, in polar solvent mixtures containing water, the proposed order of energy levels is ^{1}n,π*, ^{1}π,π*, ^{3}n,π*, ^{3}π,π*, wherein the energy levels of ^{1}π,π*, ^{3}n,π* are very close and can be exchanged.[24–27] Such an ordering of energy levels leads to interesting violations of the Kasha rule since, in some cases, photochemical reactions take place from the second excited triplet state.[24–27,36]

The photochemical reactivity of the phthalimide chromophore is very diverse in its scope. In the excited state, this chromophore undergoes intra- and intermole-

* Dedicated to Professor A. G. Griesbeck for great accomplishments in the field on the occasion of 51st birthday.

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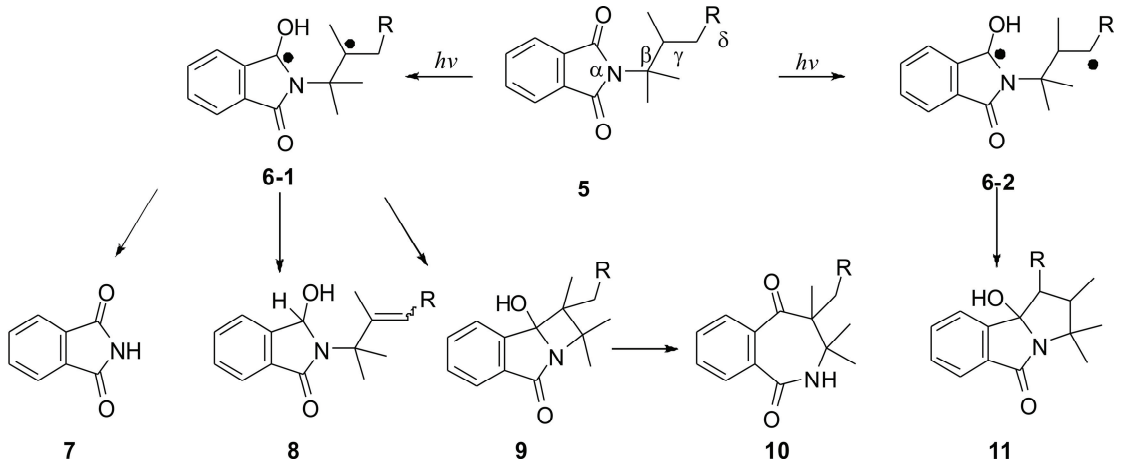
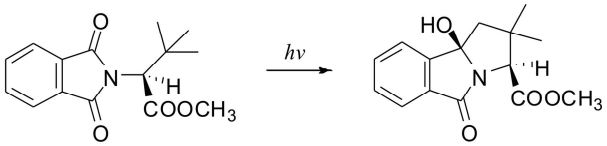


Scheme 1.

cular hydrogen atom abstraction from the suitable donor sites, which results in photoreduction, cleavage or cyclization products. In addition, the phthalimide chromophore undergoes [2+2] cycloaddition reactions that give rise to benzoazepindione products. Finally, phthalimide in its excited singlet and triplet state is a potent oxidant, and can therefore undergo single electron transfer (SET) in the presence of suitable electron-donors. Although the photochemistry of phthalimides has been reviewed several times in the past,[6–17] the aim of the present review is to give an overview of the synthetic applications of three different photoreaction pathways of phthalimides, and to point out some factors which determine their photoreactivity.

PHOTOCHEMICAL HYDROGEN ABSTRACTIONS

One of the most common reactions of compounds with a carbonyl chromophore, upon irradiation in solvents having readily abstractable hydrogen, is photoreduction. Thus, when *N*-alkylphthalimides (**1**) are photolyzed in alcohols, the reduction products **2** were obtained (R' = H 30−40 %, R' = alkyl 20−40 %), demonstrating that the photochemical behavior of carbonyl chromophore is very similar to that of simple ketones.[37] In contrast to the well-known photoreduction of benzophenones, irradiation of *N*-methylphthalimide did not furnish pinacol derivative **3**. However pinacol **3** (16−44 %), and reduction product **4** (23 %) were obtained on irradiation in the presence of a stronger H-donating agent *N*,*N*-dimethylcyclohexanamine.[6,38]



Scheme 2.

Photochemical H-abstractions on phthalimides are particularly interesting in the context of intramolecular reactions. Scheme 1 represents possible pathways after initial photoinduced intramolecular γ- or δ-H abstraction for phthalimide derivative **5**. In principle, the resulting biradicals **6-1** and **6-2** can undergo fragmentation to **7**, secondary H-transfer to give **8**, or cyclization to **10** and **11**, depending on the substitution pattern.[39] The cyclized benzazepinedione products **10** are generally obtained in low to moderate yields (5−20 %).[39]

Generally, as the rate constants for γ-H abstraction are higher by an order of magnitude than those for δ-H abstraction, the former are more readily abstracted.[1] However, δ-H abstractions are possible, and take place especially when γ-H atoms are not available. One example of synthetically applicable photochemical intramolecular δ-H abstraction is given in Scheme 2. In that example *N*-phthalimido-*tert*-leucine **12** undergoes photocyclization giving **13** (90 %), presumably *via* the singlet excited state.[40]

N-arylphthalimides are generally characterized by low quantum yields of intersystem crossing. Conse-

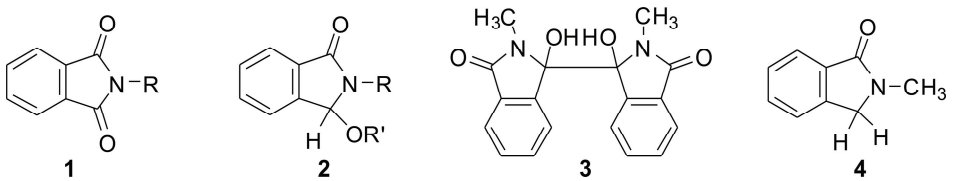
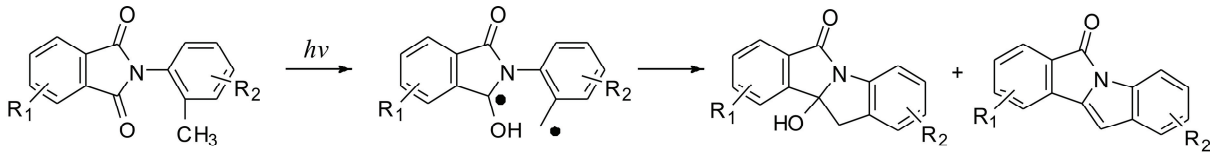
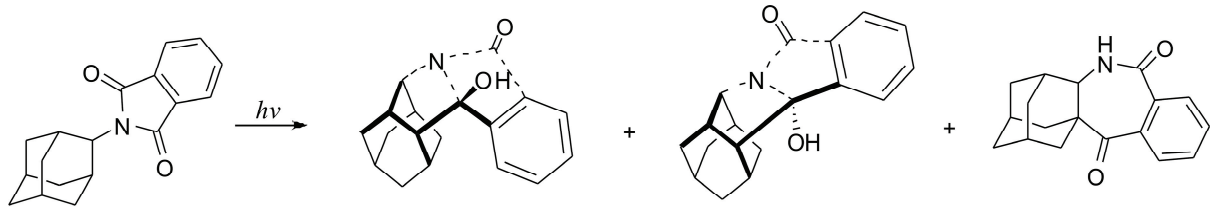


Chart 1.



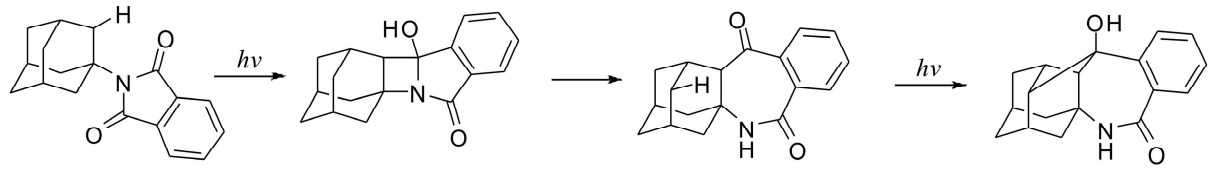
14 **15** **16** **17**

Scheme 3.



18 **19** (10 %) **20** (4 %) **21** (2 %)

Scheme 4.



22 **23** **24** (82 %)

Scheme 5.

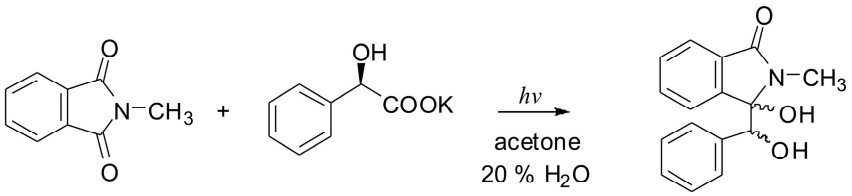
quently, photochemical reactions that originate from triplet excited states also proceed with low quantum yields. One example of photochemical intramolecular H-activation of *N*-arylphthalimides is given in Scheme 3.[41] Here, the tolyl phthalimide derivatives **14** undergo photoinduced intramolecular H-abstraction giving biradicals **15** which on combination give **16** and/or **17** (the total yield on cyclization products **16** and **17**, 20−65 %). The substituent on the phthalimide moiety R_1 has a remarkable influence on the photoreaction. The electron withdrawing substituents R_1 (CN or $COOCH_3$) facilitate the cyclization, whereas with the electron donating substituents (OCH_3 or NH_2) the reaction does not take place. Since the R_1 has a direct influence on the imide excited state, the finding was explained by an inverting of the order of the reactive lower $^3n,\pi^*$ and the nonreactive upper $^3\pi,\pi^*$ excited state. On the other hand, the substituent R_2 only influences the stability of the benzyl radical center on the adjacent phenyl ring in biradical **15**.[41]

Photoinduced intramolecular photochemical H-abstraction reactions on phthalimide derivatives have also been studied in the solid state.[42] It was found that the parameters determining photochemical reactivity for typical carbonyl compounds in the solid state[43-45] can also be extended to phthalimides. From the investigated phthalimides, *N*-(2-adamantyl)phthalimide (**18**) underwent a solid state photochemical reaction. The reaction was found to be both regio- and stereoselective, resulting in an *endo*-alcohol **20** (isolated yield 10 %). On the other hand, the photoreaction of **18** in solution gave an *exo*-alcohol **19** (10 %) as the main product together with an *endo*-alcohol **20** (4 %) and a benzazepindione **21** (2 %) (Scheme 4).[42]

Recently, we discovered also a domino photochemical reaction of two consecutive photochemical intramolecular H-abstractions. Photolysis of adamantylphthalimide **22** gives rise to a complex hexacyclic methanoadamantane benzazepine derivative **24** (82 %) *via* intermediate **23** (Scheme 5).[46]

PHOTOINDUCED ELECTRON TRANSFER REACTIONS

In the presence of good electron donors, phthalimide in the excited state does not abstract H-atoms but rather undergoes a SET. For an example, the reduction potential of *N*-methylphthalimide in the ground state in DMF is −1.37 V *vs.* SCE.[47] Thus, taking into account the energy for the excitation to the singlet, and the triplet states (E_{00} = 3.8 eV and E_{00} = 3.1 eV, respectively), the reduction potentials in the excited states are estimated to



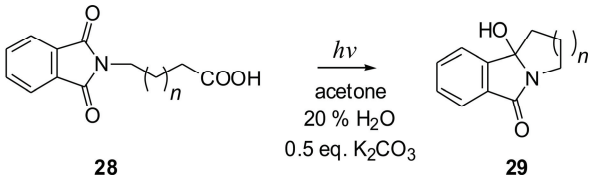
25 **26** **27** (70 %)

Scheme 6.

be 2.4 V, and 1.7 V *vs.* SCE, respectively.[12,16] The feasibility of an electron transfer process between the phthalimide and the potential electron donor can be estimated from the Rehm-Weller equation.[48] The SET process generates phthalimide radical anions which can undergo secondary reactions, and thus have broad synthetic applications.

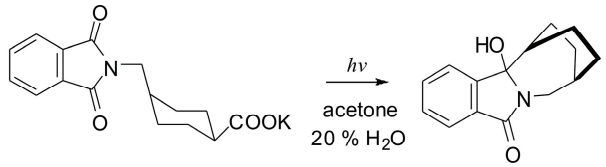
When *N*-alkylphthalimide derivatives are irradiated in polar solvents in the presence of electron-rich substrates containing a carboxylate group, an intermolecular SET takes place. The products of the SET are phthalimide radical anion and carboxyl radical, the latter of which undergoes very fast decarboxylation giving alkyl radicals.[25–27] An example of the photochemical intermolecular SET followed by the decarboxylation and an addition of the alkyl radical to the phthalimide carbonyl group is given in Scheme 6. Hydroxy acid **26** undergoes the photodecarboxylation and adds to *N*-methylphthalimide (**25**) giving mixture of diastereomers **27** in 70 % yield, but with low diastereoselectivity (52 % d.e.).[49]

Intramolecular photochemical SET-initiated decarboxylation reactions have been extensively investigated and found applications in synthesis of small and large cyclic compounds.[32–35,50,51] For example, the photodecarboxylative cyclization shown in Scheme 7 gives rise to polycyclic compounds. Depending on the chain length in acid **28** (n = 1−9), products **29** with different ring sizes can be obtained in good yields (> 75 %).[50,51] Another example is the formation of the polycyclic compound **31** from the cyclohexyl derivative **30** (Scheme 8). The polycyclic compound is obtained in 68 % yield, and the quantum yield for the product formation is 0.4.[26]



28 **29**

Scheme 7.



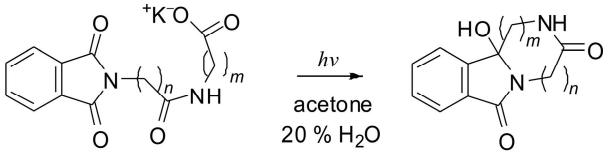
30 **31** (68 %)

Scheme 8.

Photodecarboxylative cyclization reactions have also been successfully applied in the synthesis of cyclic peptides.[33,52] Dipeptides **32** that are activated with a phthalimide moiety at the *N*-terminal have been successfully cyclized to **33** (characterized by different chain lengths n and m, Scheme 9). Besides dipeptides, cyclization was also accomplished for some tri- and tetrapeptides. The yields of cyclization are strongly dependant on the pH of the irradiated solution, as well as on the probability of intramolecular H-bonding between the phthalimide carbonyl group and the NH or COOH groups of the amino acid residues.[29,53]

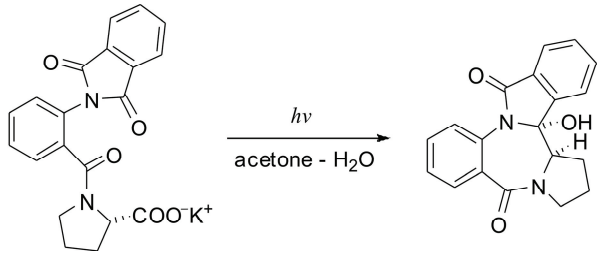
In the course of studying photodecarboxylation-induced cyclizations of the phthalimide derivatives, Griesbeck *et al*. encountered some new examples of the memory of chirality.[54,55] The concept of the memory of chirality that was introduced by Fuji and Kawabata,[56] was thus successfully applied to the photocyclization reactions of the phthalimide anthranilic acid derivatives. For example, on irradiation of the phthalimide anthranilic derivative of L-proline **34**, the photoproduct **35** was isolated in 45 % yield, characterized with high e.e. of 86 %. (Scheme 10).[54] The high degree of the memory of chirality was explained by the high activation barriers for the rotation of the 1,7-biradical intermediates about the central C−N bond, which preserves their absolute axial chirality during the course of the cyclization reaction.[54]

In addition to photodecarboxylation, photoinduced SET on phthalimide derivatives has been used to initiate cyclizations of various silyl derivatives. Mariano and



32 **33**

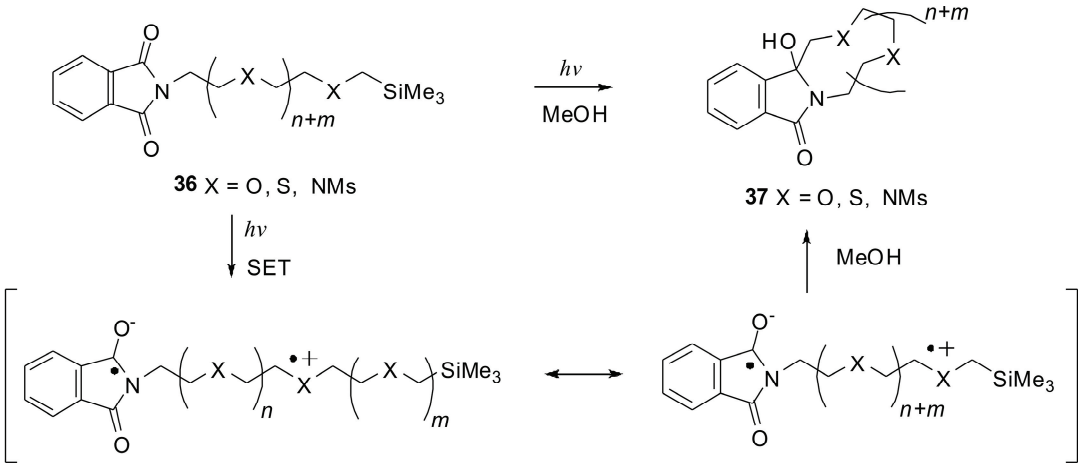
Scheme 9.



34 **35** (45 %, e.e. 86 %)

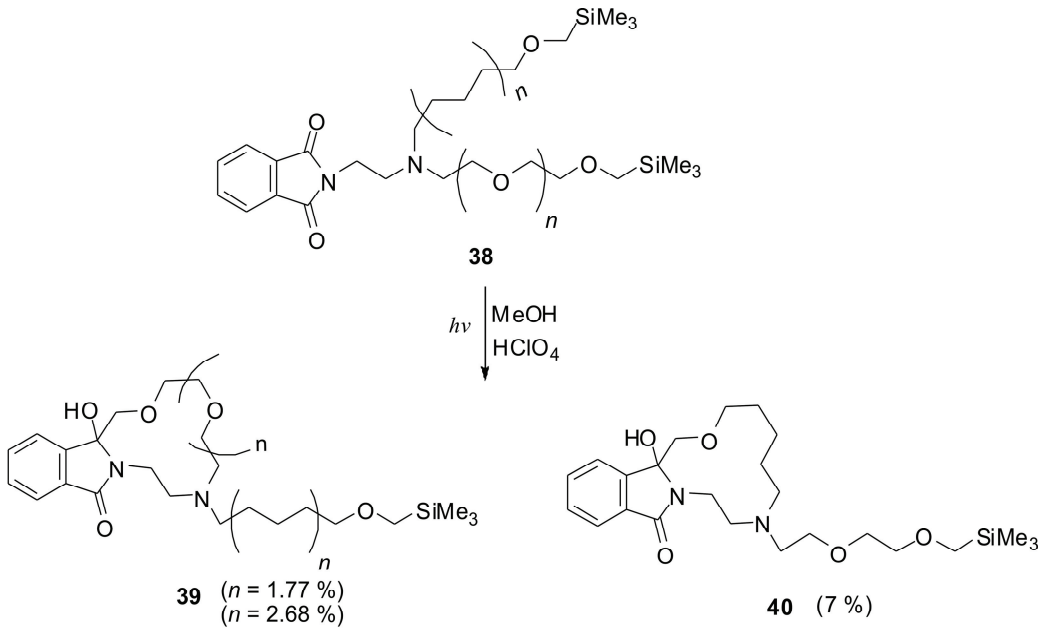
Scheme 10.

Yoon performed a systematic study of the macrocyclization of peptides and polyethers.[32–35,57] They propose that, after excitation of the phthalimide **36** and initial SET, intrasite SET leads to the eqilibiration of charge-transfer states (Scheme 11). Finally, with the suitable leaving groups (H^+, CO_2 or $SiMe_3^+$), biradicals which cyclize to **37** are obtained. The overall reaction rate and efficiency is governed by two main factors. These are (I) intrinsic rates for the heterolytic fragmentation processes (loss of H^+, CO_2 or $SiMe_3^+$), and (II) relative stabilities of the zwitter-ionic biradical intermediates.[33,34] Furthermore, Mariano and Yoon[35] have recently reported on the photocycloaddition of the phthalimide derivatives containing polyethyleneoxy and polymethylene chains (Scheme 12). Their findings suggest that polyethyleneoxy sites, which are better electron acceptors, promote the initial SET and the intrachain SET to the terminal α-trimethylsilyl ether position. Thus, irradiation of **38** in acidic methanol gave **39**, rather than **40** (Scheme 12).[35] In addition to the silyl derivatives, Mariano and Yoon developed an efficient photocyclization that has a stannyl moiety as a leaving group.[58]



36 X = O, S, NMs **37** X = O, S, NMs

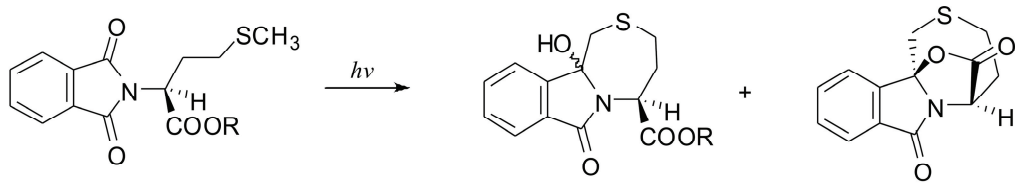
Scheme 11.



38

39 (*n* = 1.77 %) (*n* = 2.68 %) **40** (7 %)

Scheme 12.



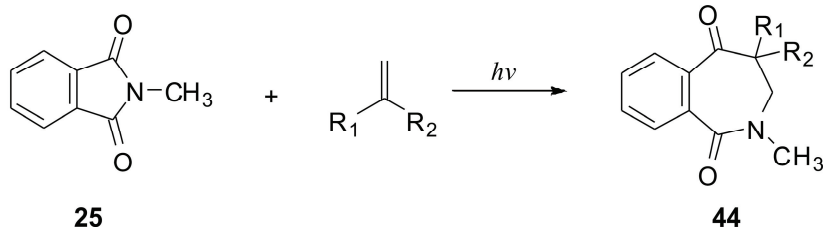
Scheme 13.

An important class of SET-induced photocyclizations of phthalimdes are those on *S*-alkylcysteine or methionine containing peptides.[25,26,59–61] Upon excitation, the SET from sulfur to phthalimide takes place, resulting in a radical ion pair that, after an H^+ transfer, gives a radical pair and a cyclization product. One example of that reaction is shown in Scheme 13. Irradiation of *N*-phthaloyl methionine methyl ester (**41**) leads to a mixture of diastereomers **42** in 84 % yield.[59] On the other hand, sensitized photochemistry of the acid derivative **41** gave diatereomers **42** (75−85 %) together with a minor amount of tetracyclic product **43**.[60]

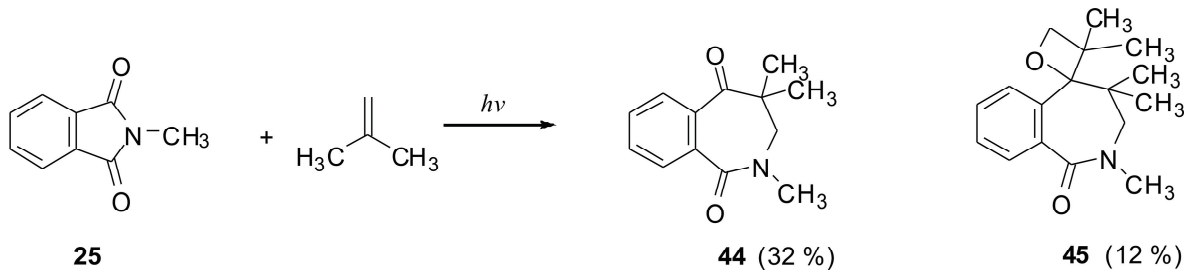
PHOTOCYCLOADDITIONS

Phthalimides can undergo several types of photocycloaddition. The most common is $[\pi^2 + \sigma^2]$ cycloaddition of the C(O)−N bond with alkenes, giving rise to benzazepinediones. Besides the oxetane furnishning [2 + 2] cycloadditions to the carbonyl group, [4 + 2] cycloaddition reactions to the aromatic ring are also possible, albeit rare.[16] When phthalimdes are irradiated in the presence of an olefin, SET or cycloaddition may take place, depending on the substitution at the olefin. Electron donating substituents decrease the oxidation potential of alkenes, so a SET mechanism can be operative. On the other hand, when the SET process is very endergonic ($\Delta G > 5$ kcal mol^{-1}), $[\pi^2 + \sigma^2]$ cycloadditions were observed.[16] One example of $[\pi^2 + \sigma^2]$ cycloaddition is shown in Scheme 14. Irradiation of *N*-methylphthalimide (**25**) in the presence of 3 equivalents of various propene derivatives gave benzazepinediones **44** in 25-67 % yield.[62,63] Irradiation in the presence of larger excesses of olefins (50 equivalents), and particularly with vinyl ethers, gave Paterno-Büchi secondary photoproducts in addition to those expected for $[\pi^2 + \sigma^2]$.[64] Scheme 15 shows the photoreaction of **25** with 2-methylpropene giving rise to azepinone **44** (32 %), as well as the product of the secondary Paterno-Büchi reaction **45** (12 %).

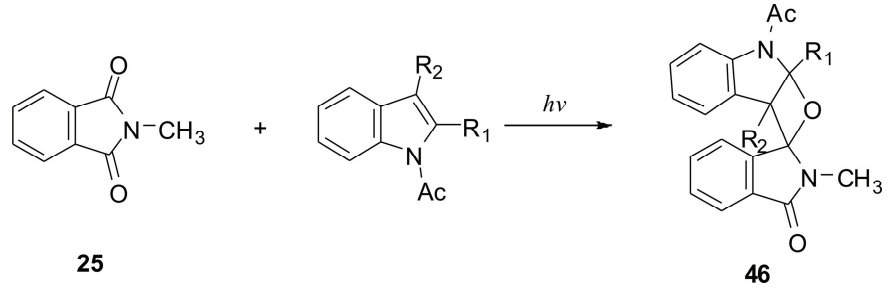
To prove the concerted reaction mechanism in the phthalimide cycloadditions, Mazzocchi et al. studied the stereoselectivity of the photoaddition to *cis*- and *trans*-2-butenes.[65,66] Stereoselective formation of *cis*-, and *trans*-banzazepinediones indicated that no intermediate



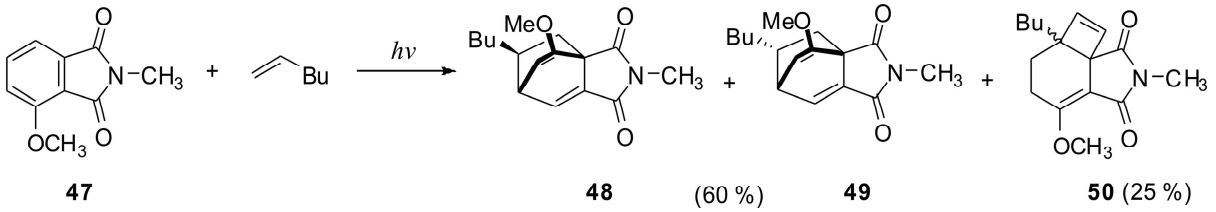
Scheme 14.



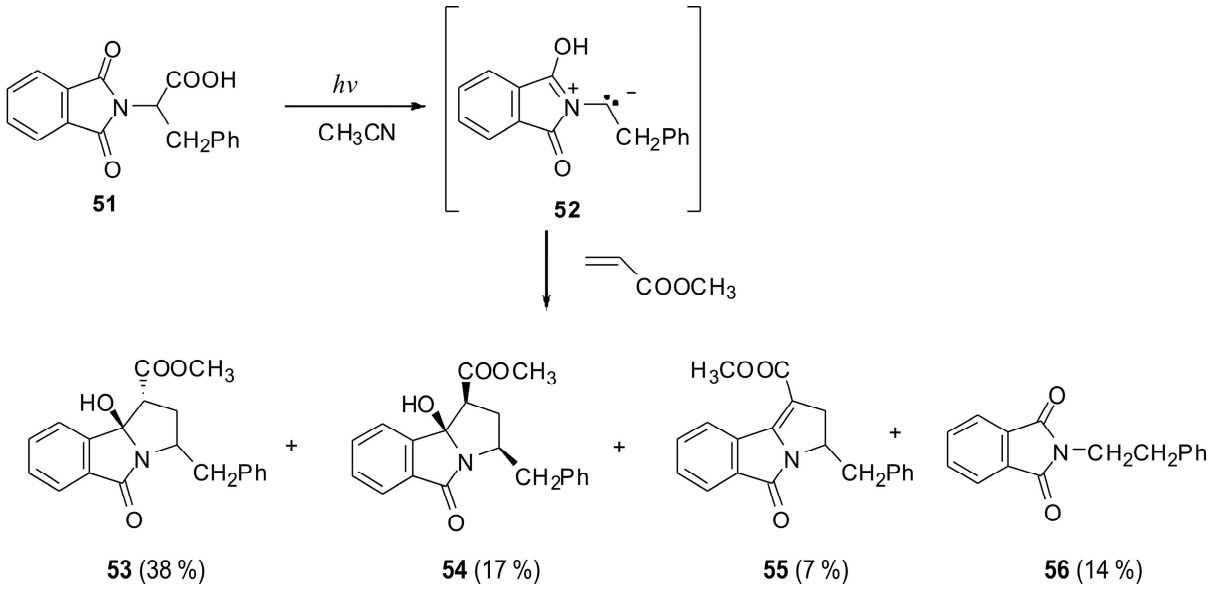
Scheme 15.



Scheme 16.



Scheme 17.



Scheme 18.

was involved.[65] Finally, Mazzocchi *et al*. reported mechanistic evidence for the concerted reaction mechanism of the cycloaddition, as judged by the regioselectivity of the cycloadditions for unsymmetrically substituted phthalimides.[66,67] The authors found that product distribution was influenced by the substituent at the phthalimde. This influence was correlated with a C(O)−N double bond character, rather than the electronic stabilization of the radical-anion on the carbonyl moiety.[67] However, after recent investigation of the formal intramolecular [5+2] photocycloaddition of maleimides by K. Booker-Milburn *et al*.,[68] the conclusion that $[\pi^2 + \sigma^2]$ cycloaddition on phthalimides proceeds *via* a concerted reaction mechanism may be questionable. For maleimides the authors suggested a mechanism of cyclization which includes initial C(O)−N bond cleavage.[68]

The Paterno-Büchi reaction of the phthalimide carbonyl moiety giving rise to the oxetane products was also reported.[69] In these cycloadditions the olefin is often sterically congested. For example, irradiation of **25** with *N*-acetyl-2,3-disubstituted indoles gave very sterically hindered oxetanes **46** in the yield of 18-62 % (Scheme 16).[70]

Examples of photochemical formal [4+2] cycloadditions were reported by Suau[71] and Kubo.[72] In the first example (Scheme 17), 3-methoxyphthalimide (**47**)

was irradiated with 1-hexene giving two *para*-cycloaddition products **48** and **49** (60 %) and one *ortho*-cycloadduct **50** (25 %). Formation of *para*-cycloadducts **48** and **49** was explained by initial [2+2] cycloaddition, followed by subsequent electrocyclic ring-opening, photoinduced [1,7] sigmatropic shift and ring closure.[71]

A special class of photocycloaddition reactions of phthalimides are dipolar cycloadditions taking place *via* photogenerated azomethine ilide intermediates.[73–76] For example, photolysis of the *N*-phthaloyl derivative of phenyl alanine **51** gives azomethine ilide **52** which, in the presence of methyl acrylate as dipolarophile, gives a mixture of products **53**-**56** (Scheme 18).[73] Product **53** is the primary photocyclization product whereas **54** and **55** are formed from **53** in a dark reaction.

CONCLUSION

Phthalimide derivatives undergo various photochemical reactions which differ substantially in their reaction mechanisms. However, the selectivity of the processes can generally be well-tuned by the choice of the appropriate photoreaction partner. Whereas the electron-rich alkenes, arenes and sulfur derivatives induce the SET processes, reactions with electron-deficient substrates give rise to cycloaddition or H-abstraction products. Generally, photochemical reactions of phthalimides are characterized by high selectivity. The stereocontrol can be controlled by the classic auxiliary-based chiral induction, or memory of chirality. Therefore, photoreactions of phthalimides can be applied in the synthesis of complex structures such as nitrogen-containing heterocycles and natural products.

Acknowledgements. We thank the Ministry of Science Education and Sports of the Republic of Croatia (grant No. 098-0982933-2911). The support of the DAAD and The Croatian Ministry of Science, Education and Sports on a bilateral project is also gratefully acknowledged.

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SAŽETAK

Fotokemija *N*-alkil i *N*-aril supstituiranih ftalimida: H-apstrakcije, reakcije prijenosa elektrona i cikloadicije

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Ftalimidna skupina je kromofor koji podliježe širokom spektru intra- i intermolekulskih reakcija. Fotoreakcije ftalimida mogu biti klasificirane u tri skupine: H-apstrakcije, cikloadicije i reakcije prijenosa elektrona. Fotoprodukti su aza-heterocikli, korisni sintoni u sintezi kompliciranih heterocikličkih i prirodnih spojeva. Svrha ove revije je dati pregled sintetske primjene fotokemijskih procesa ftalimida, kao i ukazati na parametre koji utječu na fotokemijsku reaktivnost.