Environmental Organic Photochemistry: Advances and Perspectives

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Abstract: This review is a survey of recent advances in environment related aspects of organic photochemistry. Besides presenting general concepts, the manuscript is mainly focused on the photoreactivity of natural organic matter, and on the photochemistry of anthropogenic substances under natural light irradiation.

Keywords: Environmental photochemistry, organic photochemistry, natural organic matter, photocatalysis, photodegradation, photo-oxidation.

GENERAL ASPECTS OF ENVIRONMENTAL ORGANIC PHOTOCHEMISTRY

By considering the general definition of the term "Photochemistry" internationally accepted by the chemists' community [1], one might define "Environmental Organic Photochemistry" the branch of science concerned with both the environmental effects of organic photochemical reactions [1] and the study of molecular photochemistry occurring in the environment. This includes photocatalytic processes, as defined by the more recent glossary on photocatalytic terms [2], involving organic substrates and potentially applicable for environmental remediation. Additionally, a positive effect on the environment is gained whenever in-lab or industrial photochemical synthesis of organic compounds are developed as a green chemistry approach [3]. In this context a major advance in preparative photochemistry has been achieved by Oelgemoeller's group by taking advantage of the microflow technology applied to photochemical reactions [4].

Although modern photochemistry was born in 1902 with the visionary perspective of Giacomo Ciamician [5], environmental aspects of organic photochemistry have been receiving increasing attention only in the last few decades. Indeed, in coincidence with major concerns about ozone layer reduction over the Antarctic zone, various studies have been devoted to assess the impact of Earth-reaching UV radiation on the ecosystems [6]. Indeed, these types of studies still represent a major challenge, especially considering the number of environmental parameters affecting the studied photochemical phenomenon. Therefore, the photochemical behaviour of organic substrates under natural or simulated environmental conditions are often presented either as peculiar reactivity of classes of compounds (e.g. halogenated aromatic compounds) or of generally defined mixtures such as natural organic matter (NOM), dissolved organic matter (DOM), or effluent organic nitrogen (EON). When accompanied by a complete identification of photoproducts, mechanistic hypothesis can be generalized, particularly for homogeneous classes of compounds such as halogenated phenols [7]. On the other hand, many kinetic studies have been devoted to the measurement of the degradation rate of particular substrates or homogeneous classes of pollutants. In this context, a very recent review reports a list of photoreactivity constants for a series of environmentally relevant micropollutants [8].

Besides cases where chromofore- or substituent-driven photoreactivity leads to stable photoproducts, the majority of reported studies normally concern the oxidative degradation of the substrate by means of photogenerated reactive oxygen species (ROS). Among ROS, singlet oxygen is probably the most studied from both the photophysical and photochemical reactivity aspects [9]. It can be easily formed in aqueous systems containing coloured substances as sensitizers, and its steady-state concentration, especially in surface waters, depends on several environmental parameters including temperature, depth, sunlight exposure, colored NOM's concentration (acting as potential sensitizer), and total NOM's concentration (acting as potential substrate/quencher). These aspects have been rationalized more than two decades ago concluding that for singlet oxygen's concentrations found in surface waters, only substrates containing electron rich double bonds or easily oxidazable moieties would be selectively degraded [10].

Interestingly, photochemically stable organic compounds can be "indirectly" involved in environmental photochemical processes through complexation with metal ions typically found in surface waters. For instance, environmental aspects of a series of copper complexes have been rationalized considering their role in generating various ROS [11]. More generally, metal complexes can be involved in environmental photochemistry either through electron transfer processes where the substrate is directly involved as a donor or acceptor, or through the generation of ROS in photo-fenton like processes [12].

As far as photobiological processes are concerned, photochemical aspects directly affecting the ecosystem have been rationalized, for example, for organisms such as phytoplankton, whose fate is strongly depending also on light exposure [13]. However, the majority of environmental photochemistry studies regards the impact of anthropogenic substances such as pesticides, drugs (and their metabolites), and cosmetics, associated with light exposure under natural or simulated environmental conditions.

For pesticides, local and international legislation may regulate their use, therefore limiting their environmental concentration. Nevertheless, studies on their potential involvement in environ-

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mental photochemistry are still needed, together with the assessment of new pesticides photodegradability [14, 15].

For drugs and their metabolites, instead, concentrations reaching surface waters strongly depend on each drug's popularity and widespread use. Additionally, for years pharmaceutical companies have worked on improving their drug's photostability in order to avoid short shelf-life of their products, thus obtaining compounds which are more environmentally persistant. For these reasons, the environmental fate of drugs have become more and more a prioritary issue, also considering the development of microbial resistance against widely used antibiotics. In a recent review on this aspect, also photochemical processes are taken into account as one of the major pathway of the environmental degradation of antibiotics [16]. Moreover, the toxicity of photoproducts generated by photolysis under natural conditions of widely used pharmaceuticals in surface waters is today an additional concern [17].

Another major, but often underestimated threat, regards the photochemistry of cosmetics, including sunscreen and other personal care products, which easily and abundantly reach surface waters during bathing seasons coinciding with higher sunlight irradiation. In this context, valuable model for ecological risk assessment related to sunscreen components, have been recently proposed by combining experimental data and theoretical photoreactivity studies [18].

Environmental reaction media for the photochemistry of organic compounds strongly depend on organic compound/pollutants mobility [19]. Typical media are surface waters (lakes, rivers, marine environment, etc.) [10, 20-23] and atmosphere [24-26]. More recent studies regarded the photochemistry at the gas/liquid interface, such as in aerosols in the Arctic haze [27] or from motor vehicle and plants emissions [28], and gas/solid interface, such as the photochemistry in soils, which strongly depends on soil thickness and light penetration [13, 29]. Following the pioneering study on monochlorophenols [30], a more recent field of investigation concerns environmental photochemistry in the ice matrix, which is at the borderline of solid phase and solution photochemistry, with the possible involvement of photoinduced proton transfer from the frozen solvation shell [30-32]. These aspects have been further investigated also by using computational data in the attempt of validating a model based on the photochemistry of organic molecules in artificial snow grains [33].

In addition to the above issues, the recent development of nanotechnologies based on fullerenes, graphene, and carbon nanotubes (CNTs), raises questions about the environmental impact of these new photoactive materials, whose photoreactivity and role in generating ROS under natural environmental conditions needs still to be fully addressed [34-36].
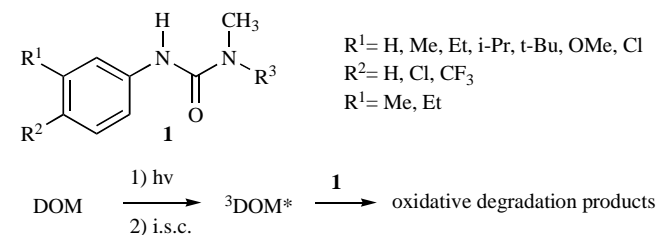
Besides studying the effect of photochemical reactions in the environment, environmental photochemistry includes the development of photochemical technologies for air or water remediation.

A recent review about the exploitation of photochemical technologies for indoor air purification from VOCs has been recently published by Wang's group [37]. Moreover, a plethora of articles reporting photocatalytic studies of potential environmental application, mostly based on titania derived photocatalysts [38] and photofenton processes [38], also coupled to biological degradation [39, 40], have been published and recently reviewed. On the other hand, organic photocatalysis, which includes the use of covalently linked [41] or ionically exchanged [42] supported photosensitizers, has been very recently reviewed [43]. For these reasons, photocatalytic processes have been considered in this review only when crucial to explain photodegradation patterns of anthropogenic organic compounds.

PHOTOCHEMISTRY OF NATURAL OR DISSOLVED ORGANIC MATTER (NOM/DOM) UNDER NATURAL OR SIMULATED ENVIRONMENTAL CONDITIONS

The photochemical behavior of chromophoric dissolved organic matter (CDOM) has been attentioned since mid 90's [44] both in marine and riverine waters [45], and has been studied by following the decrease of UV absorption at 280-300 nm ascribed to the degradation of chromophoric substances. Later on, the role of colored DOM in promoting the degradation of phenylurea-based herbicides **1** (Scheme **1**) in lakes has been rationalized in terms of an initial one-electron oxidation involving an excited triplet states of the chromophoric substances [46].

R^1= H, Me, Et, i-Pr, t-Bu, OMe, Cl
R^2= H, Cl, CF_3
R^1= Me, Et

$$DOM \xrightarrow[\text{2) i.s.c.}]{\text{1) hv}} {}^3DOM* \xrightarrow{\textbf{1}} \text{oxidative degradation products}$$
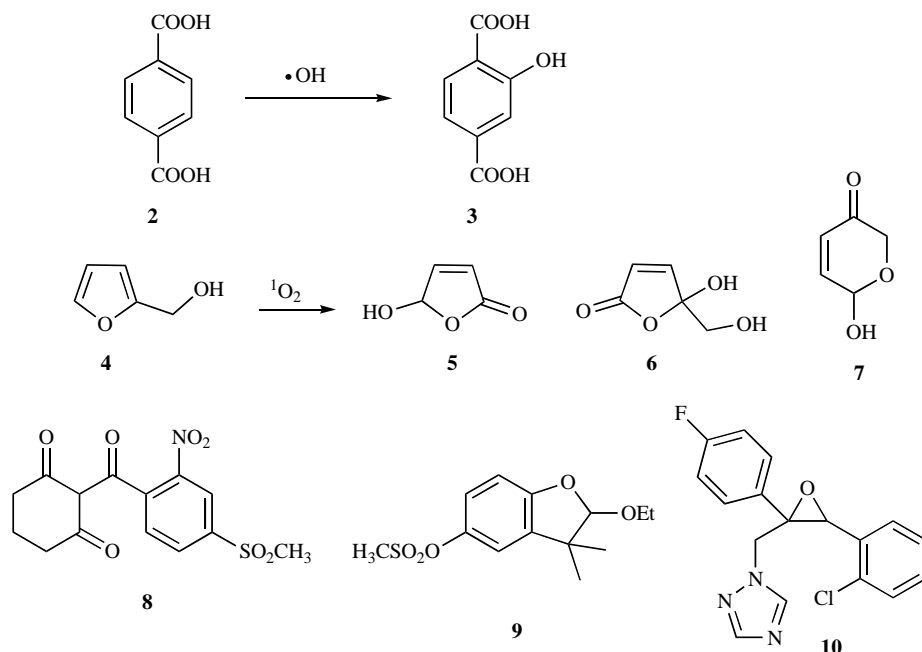
Scheme 1.

Very recently, an interesting correlation between CDOM's photoactivity and lake's surroundings was based upon a principal components analysis of the reactivity of 2,4,6-trimethylphenol (TMP) used as molecular probe [47].

The photocatalytic activity of NOM, was recently evaluated by measuring the rate of production of various ROS, from irradiated suspended compost under simulated solar light. Hydroxyl radical production was measured by monitoring the reactivity of terephtalic acid **2**, whilet the production of singlet oxygen was monitored by using furfuryl alcohol **4** as a probe. Both series of data were then compared with the activity of irradiated compost in promoting the degradation of pesticide micropollutants such as mesotrione **8**, ethofumesate **9**, and epoxiconazole **10** (Scheme **2**) [48].

In many cases, humic acids (HA) have played their role in affecting the photoreactivity of natural organic matter under environmental conditions, for instance by acting as sensitizers for singlet oxygen production. Due to the complexity of their composition, it is difficult to identify specific components of HA as being responsible for the observed photoreactivity. Nevertheless, studies aiming at identifying the role of specific components of HA such as phtalocyanine-like substances, are starting to appear in recent literature [49].

Very recently, the involvement of NOM in the photochemical generation of organomercurial species has been claimed to occurr through an initial Hg(II) complex formation with typical oxygenated organic compounds (alcohols and carbonyl compounds), followed by a methyl transfer/photo-alkylation process [50]. Other recent photoreactivity studies of naturally occurring substances have regarded the degradation kinetics of a series of isoflavone phytoestrogens [51] and the impressive identification of hydroxyl radical promoted photodegradation products of cylindrospermopsin (Scheme **3**) [52].

On the other hand, studies aimed at forcing the degradation of NOM by using high-energy UV radiation, also in combination with hydrogen peroxide [53]. However, while these studies complete the
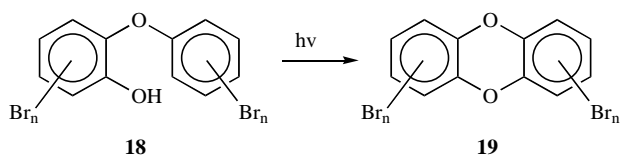
Scheme 2.
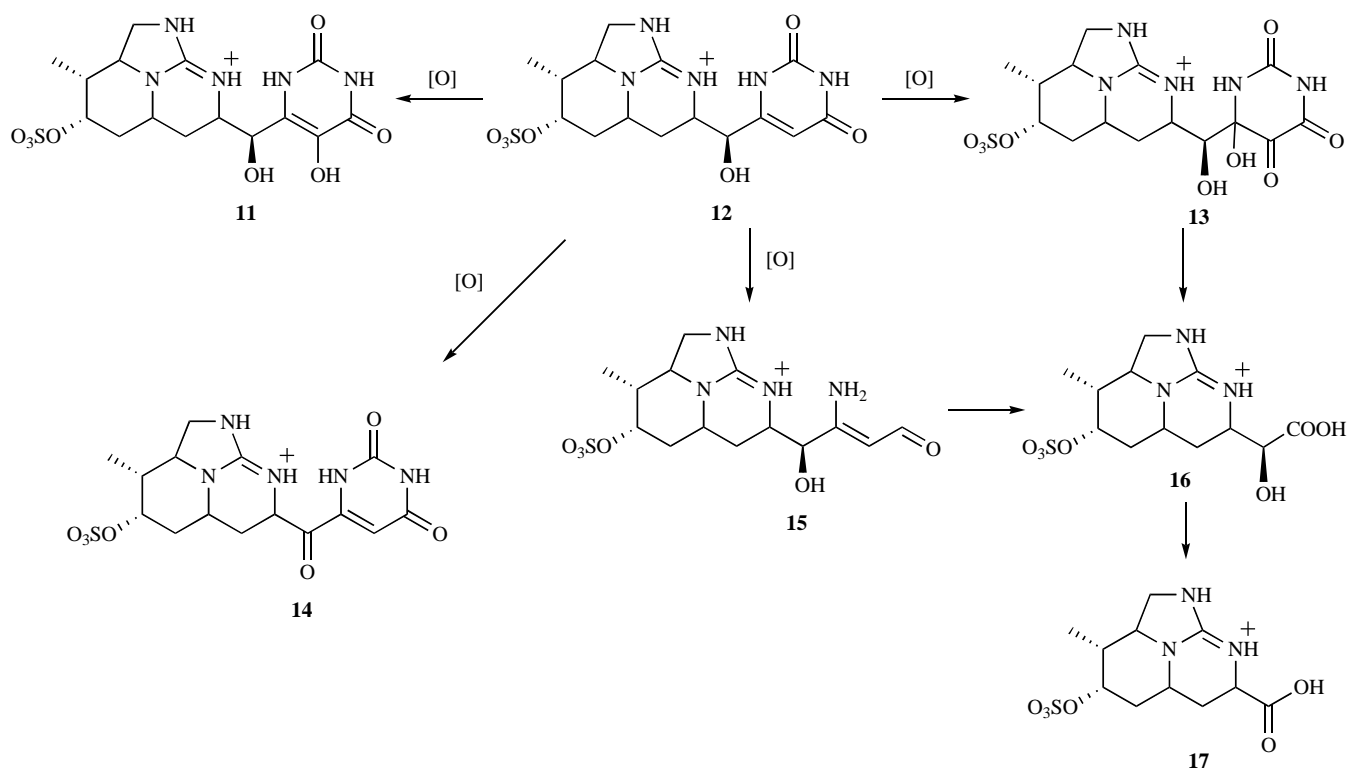
Scheme 3.

frame of NOM's photodegradability approaches, the feasibility of such procedure for practical water treatment is technologically questionable.

PHOTOCHEMISTRY OF ANTHROPOGENIC ORGANIC COMPOUNDS UNDER NATURAL OR SIMULATED ENVIRONMENTAL CONDITIONS

The production and disposal of environmentally persistant compounds has been, and likely will continue to be, one of the major threat for the ecosystem. In this context, the research towards photostable bioactive molecules and the social need for bio/photodegradable materials/substances represents one of the modern "environmental photochemistry conundrum". In this context, several studies have been devoted to enhance the photodegradation kinetics of potentially harmful substances, however only a limited amount of investigations report a complete identification of photoproducts and their toxicity. For example, polychlorinated benzenes (PCBs) and nitrobenzenes (PCNBs) remained unchanged under sunlight irradiation, but were photochemically degraded under reductive conditions [54].
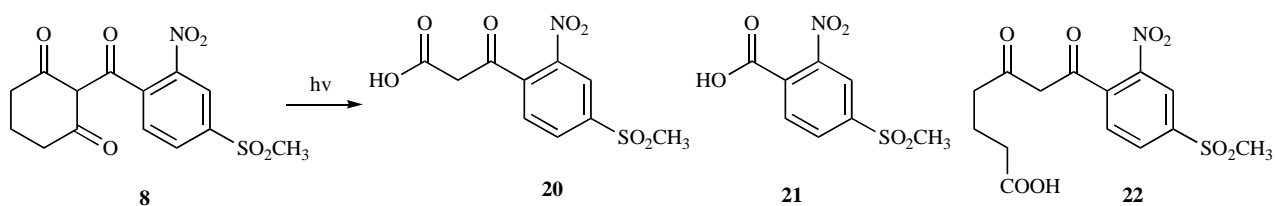
On the other hand, while ideally the oxidative photodegradation of organic compounds should lead to complete mineralization into carbon dioxide and water, in the worst case scenario, photoactive compounds will be transformed, under natural environmental irradiation conditions, into more persistent and stable harmful compounds. The latter case is for example represented by the oxidative phototransformation of polybrominated diphenylethers leading to the corresponding dioxins (Scheme 4) [55-59].
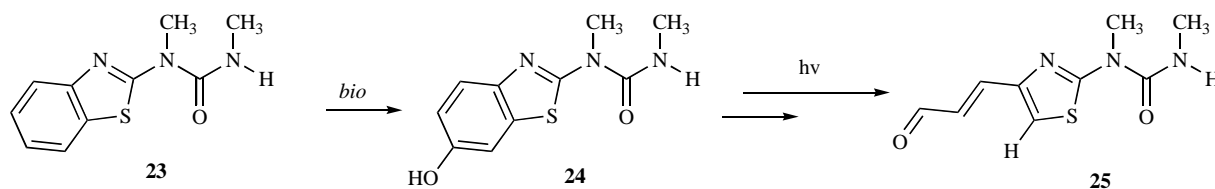

Scheme 4.

As for the degradation of pesticide compounds, the photoproducts resulting from the irradiation of mesotrione **8** in acqueous media have been identified by HPLC-ESI-MS [60].
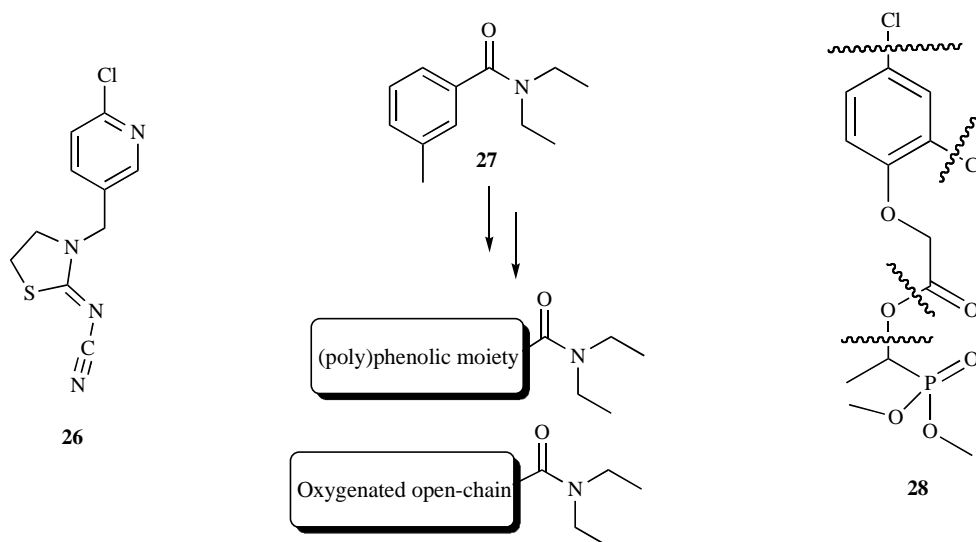
Similarly, the degradation of urea-based pesticide MBTU **23** has been investigated in one of the pioneering studies about the coupling of biotransformation with photochemical remediation (Scheme **6**) [61].

Interestingly, a recent investigation on the photoreactivity of two-component herbicide mixtures, containing nicosulfuron and mesotrione **8**, showed the mixture having an accelerating effect on both herbicide decay rates [62]. Other recent kinetic studies have regarded the photooxidative degradation of thiachloprid insecticide **26** [63], of the DEET (N,N-diethyl-m-toluamide) mosquito repellant **27**, whose oxidative degradation mostly involves the raromatic ring opening leaving the amido moiety intact [64], and of the new herbicide HW-02, whose photofragmentation pattern was however studied in organic solvents (Scheme **7**) [65].

A recent study by Vione, Minero and coworkers, showed that the presence of competing dissolved organic compounds (DOC) negatively affects the photodegradation of 4-chloro-2-methylphenoxy- acetic acid (MCPA) through its direct photolysis, thus increasing the relevance of alternative photodegradation pathways involving hydroxyl radical as reactive species [66]. Several other studies from the same group aimed at modeling the photodegradation of pollutants in surface waters by using variously substituted nitrophenolic compounds **29-31** as model substrate (Scheme **8**) [20-22].

A classes of compounds whose photochemical behavior in open water has been almost neglected is that of antifouling agents. In one of the very few studies in this field, the photoreactivity of Sea-Nine
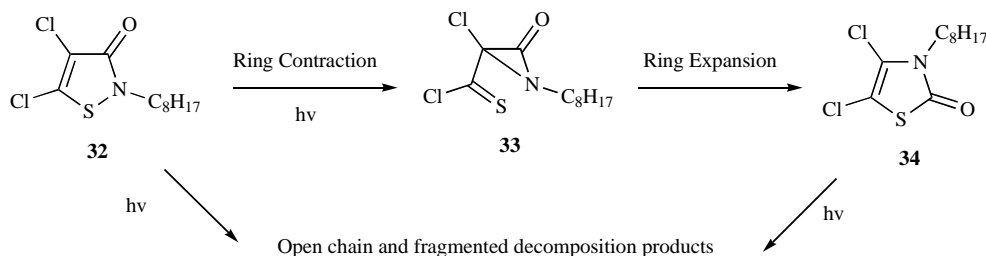

Scheme 5.
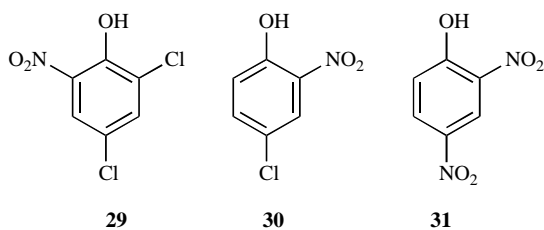
Scheme 6.

Scheme 7.

Scheme 8.

211 **32** (Scheme **9**) was investigated in different types of water, and the relative photodegradation kinetic parameters were showing a higher photodegradability in naturally occurring acqueous environment than in distilled water [67]. The observed photoreactivity involved also a *Ring Contraction – Ring Expansion* (RCRE) rearrangement into the corresponding thiadiazole system **34**, a typical rearrangement of five-membered heterocyclic compounds possessing a weak O-N or S-N photolabile bond (Scheme **9**) [68].

Besides agrochemicals, pharmaceuticals are the other major class of synthesized organic compounds whose photochemical be-
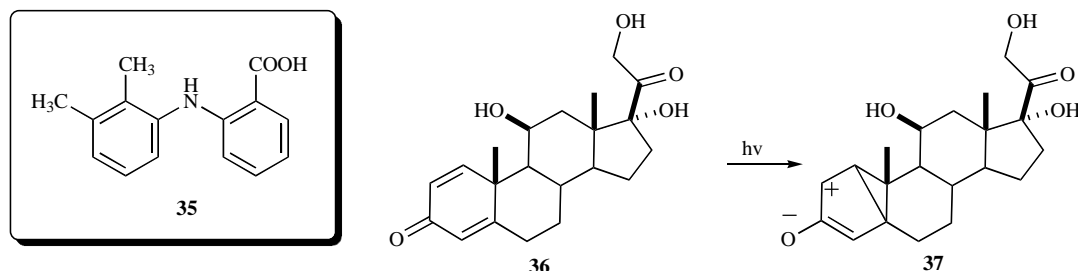
havior in the environment has been increasingly attentioned. Earlier studies regarded their presence in sewage treatment plants and their resistance to abiotic photodegradation [69]. Subsequent studies regarded widespread classes of drugs such as the non-steroidal anti-inflammatory mefenamic acid **35** [70], and steroidal derivative prednisolone **36**, whose photochemical reactivity involves a di-π-methane rearrangement into zwitterionic intermediate **37** as initial step (Scheme **10**) [71].

"Once popular" antimicrobials such as triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) **38** have shown a relevant photoreactivity, with formation of even more harmful dioxin compounds, similarly to the previously mentioned reactivity of polybrominated phenylethers [72, 73].
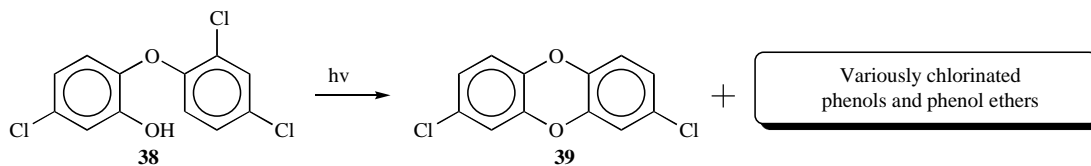
Also sulfa drugs, such as representative sulfamethazine **40**, have been investigated as photochemically degradable pollutants undergoing loss of sulfur dioxide, a major photodegradation pathway which was enhanced in natural waters due to triplet sensitization by colored DOM (Scheme **12**) [74].
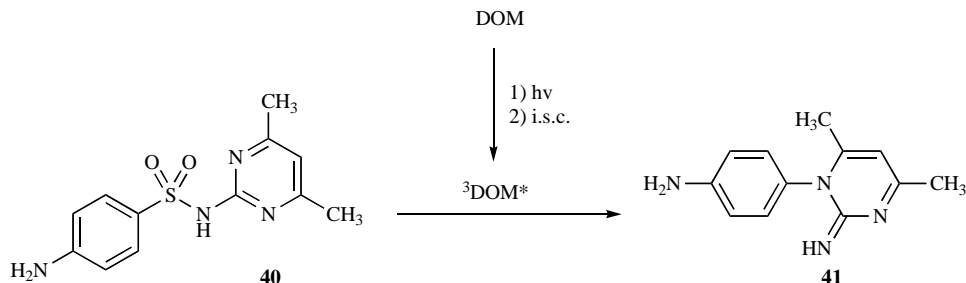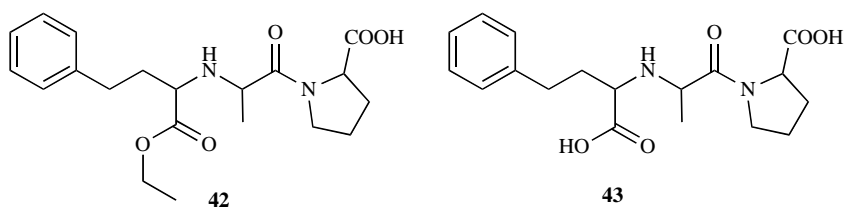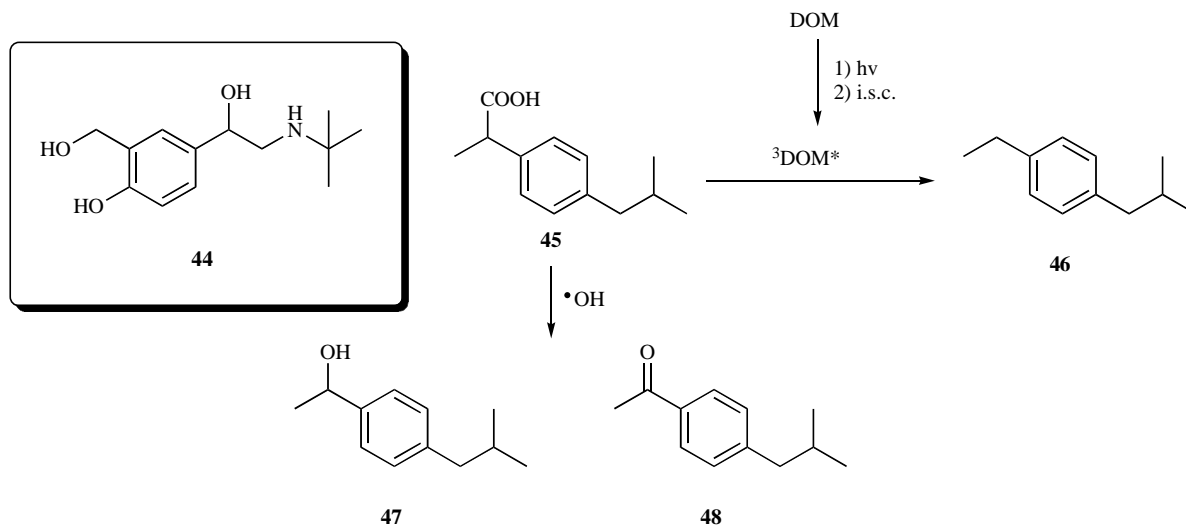

Scheme 9.

Scheme 10.

Scheme 11.

Scheme 12.

42

43

Scheme 13.

44

45

46

DOM

1) hv
2) i.s.c.

^{3}DOM*

•OH

47

48

Scheme 14.

49

50

51

$^1O_2$

•OH

52

53

+

54

+

55

56

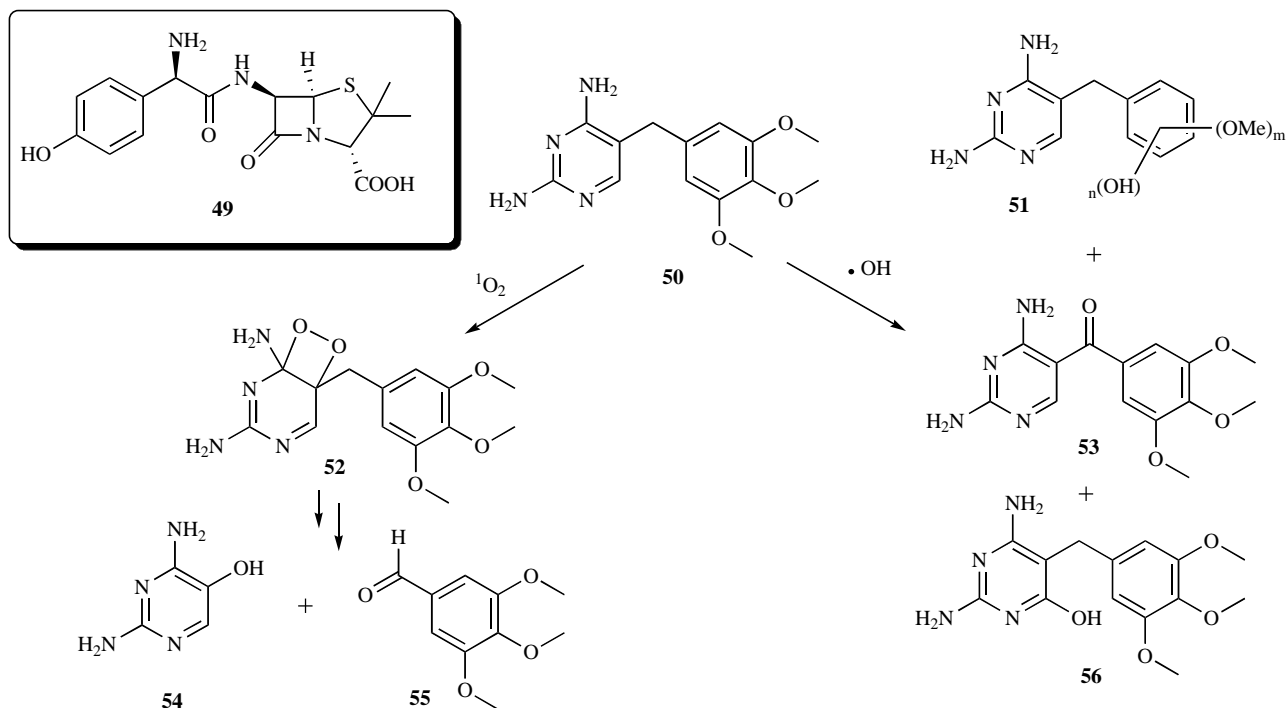**Scheme 15.**

Advances in the qualitative determination of photoproduct mixtures in complex environmental matrices have been accomplished also with the development of more performing analytical instruments, such as high resolution mass spectrometry coupled with chromatographic separation. By taking advantage of these techniques, the simulated environmental photodegradation pathway of enalapril **42** and its metabolite enalaprilat **43** could be elucidated [75].

Studies on the photoinduced degradation of other pharmaceuticals include an investigation on the photochemical behavior of salbutamol **44** which, regardless of medium's acidity, undergoes photochemical transformation under irradiation in the solar spectrum [76]. More recently, the photodegradation pathway of the popular and worldwide used antiinflammatory ibuprofen **45**, has been investigated evidencing the formation of reduced and decarboxylated

products, although contrasting results about the preferred pathways needs to be more accurately assessed (Scheme **14**) [77].

The final part of this section is dedicated to the recently emerged question of antimicrobial's use and misuse and their environmental impact in terms of multidrug resistance development. In fact, the raise of the so-called superbugs, i.e. bacteria which are resistant to a variety of clinically used antibiotics, can be contrasted by developing new antimicrobials that overcome multi-drug resistance [78]. Nevertheless, resistance towards these new drugs will eventually occurr in time. Release in the environment of such drugs

or their metabolites increases the risk of developing multidrug resistance by selecting sensitive strains. Therefore a fast removal, i.e. degradation, of these stable pharmaceuticals from surface waters is still envisaged as a major challenge. Besides classical beta lactams such as amoxicillin **49** [79], these aspects involve particularly new classes of antibiotics such as the bacteriostatic antibiotic trimethoprim **50** (Scheme **15**) [80, 81], macrolides [82, 83], fluoro-quinolones (representatively illustrated by enrofloxacin **57** in Scheme **16**) [84-87], and oxazolidinones (Scheme **17**) [88], including their newly developed derivatives [89].

Scheme 16.

$R = C(=S)OCH_3;\ C(=S)NH_2;$
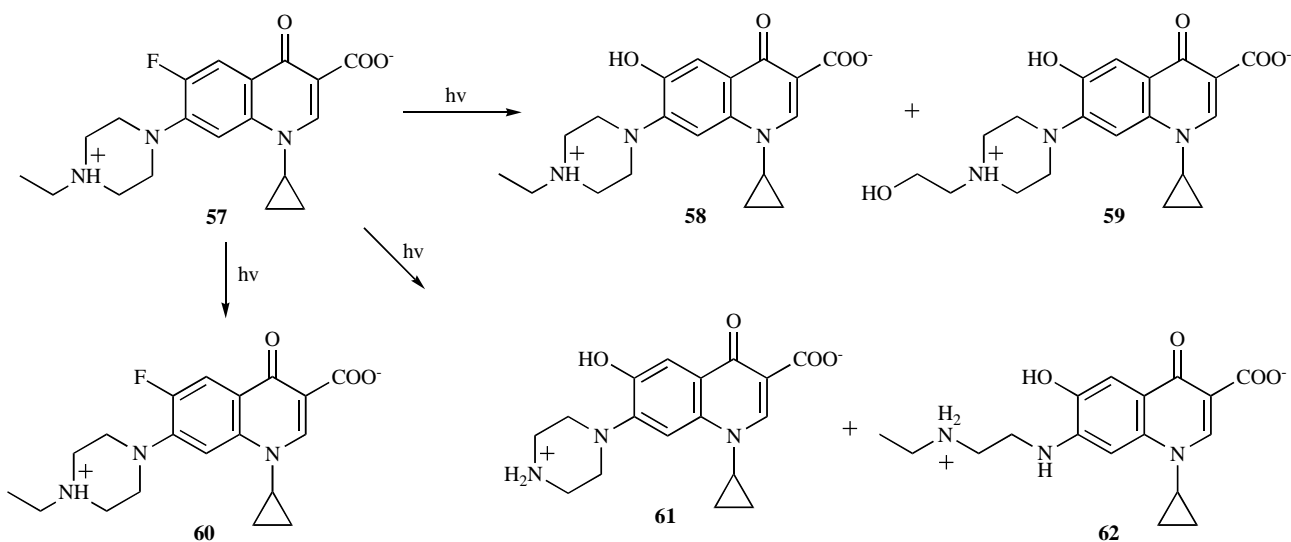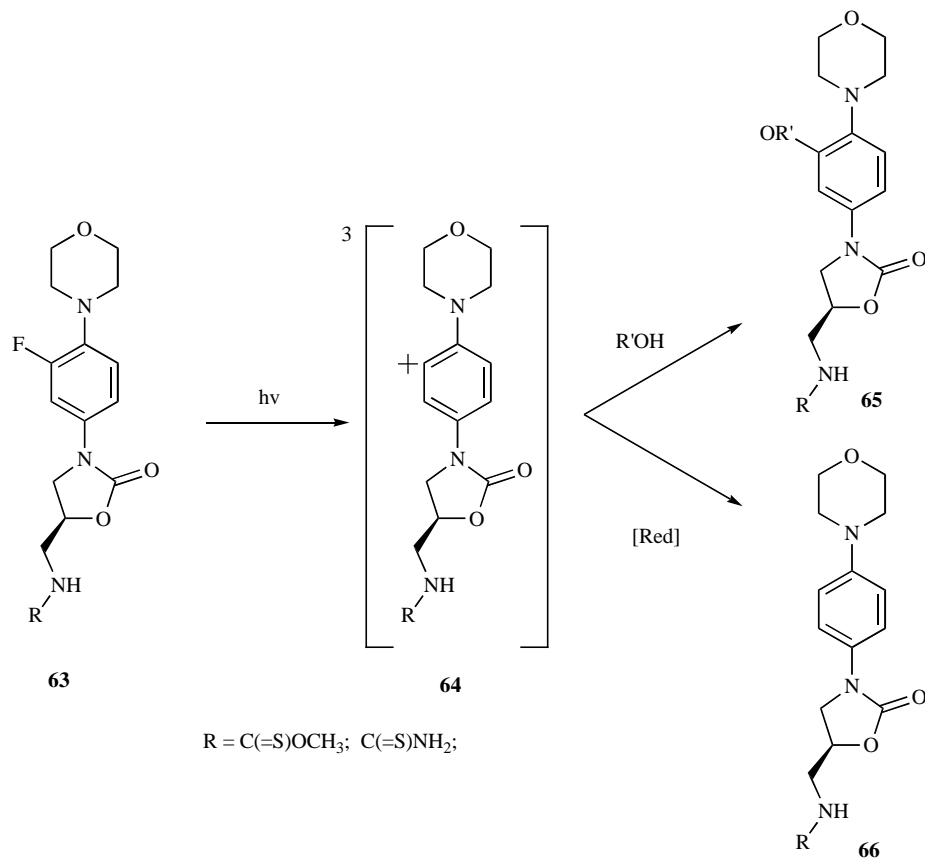
Scheme 17.

Interestingly, linezolid-like derivatives **63**, react through a photogenerated triplet phenyl cation, which can follow either a solvolytic or a reductive pathway towards derivative **65** or **66**, respectively.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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