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Research Article

Photochemical Behaviour of Carbamates Structurally Related to Herbicides in Aqueous Media: Nucleophilic Solvent Trapping versus Radical Reactions

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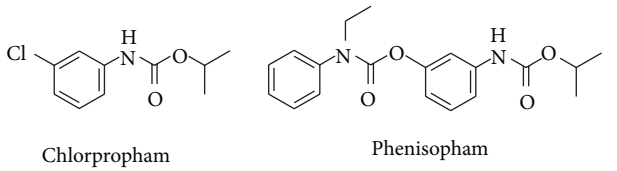
Irradiation of *N*-aryl *O*-aryl carbamates has been carried out in H_2O/CH_3CN (1 : 1 v/v) solutions at $\lambda > 290$ nm. When chlorine is on the *N*-aryl ring, halogen-substituted products are found. These photoproducts derive from the trapping of the intermediate radical cation by water and, even, by acetonitrile leading to phenols and *N*-arylacetamides (photo-Ritter products), respectively. Unsubstituted *N*-aryl carbamates slowly undergo photo-Fries reaction.

1. Introduction

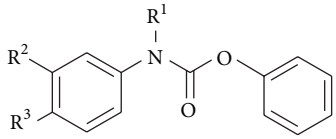
Interaction of light with matter is one of the most important processes responsible for abiotic transformations of a xenobiotic in the environment, mainly in surface water [1–3]. Often the transformation process forms products that are more toxic than the parent compound [4–7]; hence, there is a need to consider transformation products during the environmental risk assessment process [8]. Although the photochemical behaviour of a molecule depends on the presence of peculiar functional groups, given the heterogeneity and, often, the structural complexity of these pollutants, it is frequently difficult to predict or rationalize their photochemical behavior. Carbamate function is present in a wide number of biologically active compounds. In particular, carbamate pesticides are an important group which are widely used through the world [9]. Although weak, carbamates exhibit absorption of radiation present in sunlight (>290 nm), and this requires the understanding of their photochemical behaviour [10]. The most general photochemical event, mainly observed in *O*-aryl derivatives, leads to rearranged products, via photo-Fries reaction and/or fragmentation [10, 11]. Less frequent is this type of photorearrangement in *N*-aryl carbamates [12, 13]. Recently, we studied the photochemical reactivity of two carbamate herbicides, chlorpropham, and phenisopham (Scheme 1) [14].

Irradiation of phenisopham in aqueous solution at 310 nm led to photo-Fries rearranged products involving the cleavage of *O*-aryl *N*-aryl carbamate function. As observed in other cases [12], the *O*-alkyl *N*-aryl carbamate was unreactive, and this result was also found in the irradiation of chlorpropham. In the latter case the *N*-aryl moiety reacted and gave isopropyl 3-hydroxycarbanilate by photosubstitution of aryl chlorine with a hydroxyl group [12, 14]. For the two pesticides different phototransformations were observed [14]. These results induced us to gain more information about the photochemical reactivity of *N*-aryl *O*-aryl carbamates that combine functions present in the pesticides examined. In particular, we prepared six model compounds **1** (Figure 1) and focused our attention on the photoproducts formation in aqueous solution (H_2O/CH_3CN 1 : 1 v/v to have clear solutions) under UVB irradiation (>300 nm) in order that our investigation may be more relevant to environmental studies.



Chlorpropham Phenisopham

Scheme 1



1

	R^1	R^2	R^3
a	H	Cl	H
b	Et	Cl	H
c	H	H	Cl
d	Et	H	Cl
e	H	H	H
f	Et	H	H

Figure 1: Synthetic carbamates investigated.

2. Materials and Methods

2.1. Samples and Reagents. Aniline, 3-chloroaniline, 4-chloroaniline, and *N*-ethylaniline were purchased by Alfa Aesar. 3-Chloro-*N*-ethylaniline, 4-chloro-*N*-ethylaniline, and phenyl chloroformate were purchased by Sigma-Aldrich. All chemicals were used without further purification.

Milli-Q water (Millipore) was used to prepare aqueous solutions. Acetonitrile was of HPLC grade (Sigma-Aldrich).

2.2. Analytical Instruments. HPLC experiments were carried out on an Agilent 1100 HPLC system, equipped with an UV detector (set at 230 nm), using a RP-18 column (Gemini, 5 μm, 110 A, 250 × 4.6 mm). A mixture of A (H_2O containing 1% formic acid)/B (CH_3CN) 1 : 1 (v/v) was used as mobile phase at a constant flow rate of 0.8 mL/min. Analytical and preparative TLC was made on Kieselgel 60 F_{254} plates with 0.2 mm and 0.5 or 1 mm layer thickness, respectively (Merck).

Proton NMR spectra were recorded on a Varian Inova-500 instrument operating at 499.6 MHz and referenced with deuterated solvents ($CDCl_3$). Electronic impact mass spectra (EI-MS) were obtained with a GC-MS QP5050A (Shimadzu) equipped with a 70 eV EI detector. UV-Vis spectra were recorded with a Varian Cary 300 UV-Vis spectrophotometer. Melting point determinations were performed by a Gallenkamp melting point apparatus.

*2.3. Synthesis of Diaryl Carbamates **1**.* In a typical experimental procedure, to a solution of each aniline (15 mmol) in dry dichloromethane (26 mL), 1.6 mL of phenyl chloroformate (13 mmol) was added dropwise. The mixture was stirred at 0°C for 1 h and then it was kept at room temperature for 30 min. The reaction mixture was neutralized with a saturated solution of sodium hydrogen carbonate and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine, dried with anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using light petroleum/diethyl ether 7 : 3 v/v (compounds **1c** and **1e** were purified using light petroleum/EtOAc 7 : 3 and 9 : 1 v/v, resp.) to give carbamic compounds **1** with yields generally >95%. Products **1a**, **1c**, **1e** [15], and **1f** [16] were identified by comparison of their NMR spectra with those reported in the literature. The new products **1b** and **1d** were characterized on the basis of their spectral data.

*Phenyl N-3-Chlorophenyl-N-ethylcarbamate (**1b**).* Oil; EI-MS *m*/*z* 275, 182, 153; UV λ_{max} (H_2O/CH_3CN 1/1) nm 236 (log ε 3.7); ^{1}H NMR ($CDCl_3$) δ 7.36–7.17 (m, overlapped signals, 9H), 3.83 (br q, 2H), 1.25 (br t, 3H).

*Phenyl N-4-Chlorophenyl-N-ethylcarbamate (**1d**).* mp 75.9–76.7°C (hexane/ethyl acetate); EI-MS *m*/*z* 275, 182, 153; UV λ_{max} (H_2O/CH_3CN 1/1) nm 238 (log ε 4.1); ^{1}H NMR ($CDCl_3$) δ 7.38–7.25 (m, overlapped signals, 6H), 7.18 (t, J = 7.3 Hz, 1H), 7.10 (br s, 2H), 3.81 (br q, 2H), 1.23 (br t, 3H).

2.4. Photolysis Experiments. Irradiation was conducted in a Helios Italquartz multirays merry-go-round photoreactor equipped with six 15 W UV-B lamps with a maximal output at *ca.* 310 nm (1 mW cm^{-2}). Samples were irradiated in quartz tubes (20 × 1 cm, 25 mL). 1 × 10^{-3} M solutions of each carbamate **1** (50–90 mg) in H_2O/CH_3CN 1 : 1 v/v were irradiated and analyzed by HPLC and ^{1}H NMR at different times. The irradiation experiments were not stopped until starting compound was degraded at least for 20–30%. The content of all tubes was collected and evaporated. The residue was analyzed by ^{1}H NMR and then chromatographed using light petroleum/Et_2O 6 : 4 v/v. Percentages of photoproducts in the irradiation mixtures were deduced by integration of isolated NMR signals and confirmed by chromatography. Compounds **2a** [17] and **5c** (=**1e**) [15] were identified by comparison of their NMR spectra with those reported in the literature while compounds **2c**, **3c**, **8f**, **9f**, and 4-hydroxybenzoic acid (**7**) were identified by comparison of their proton NMR spectra with those of authentic samples (Aurora Building Blocks and Aldrich).

2.5. Spectroscopic Data for New Photoproducts

*Phenyl N-3-Acetamidophenylcarbamate (**3a**).* Oil; EI-MS *m*/*z* 270, 176, 134, 94; UV λ_{max} (H_2O/CH_3CN 1/1) nm 228 (log ε 3.8); ^{1}H NMR ($CDCl_3$) δ 7.75 (br s, 1H), 7.39 (t, J = 7.9 Hz, 2H), 7.29–7.22 (m, 4H), 7.18 (d, J = 7.5 Hz, 3H), 7.04 (br s, 1H), 2.16 (s, 3H).

*Phenyl N-Ethyl-N-3-hydroxyphenylcarbamate (**2b**).* Oil; EI-MS *m*/*z* 257, 164, 136; UV λ_{max} (H_2O/CH_3CN 1/1) nm 275 (log ε 3.4); ^{1}H NMR ($CDCl_3$) δ 7.38 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 4.5 Hz, 2H), 6.87 (d, J = 7.9 Hz, 1H), 6.78 (s, 1H), 6.72 (d, J = 7.8 Hz, 1H), 3.80 (br q, 2H), 1.24 (br t, 3H).

*Phenyl N-3-Acetamidophenyl-N-ethylcarbamate (**3b**).* Oil; EI-MS *m*/*z* 298, 205, 177, 135; UV λ_{max} (H_2O/CH_3CN 1/1) nm 275 (log ε 3.2), 244 (log ε 4.0); ^{1}H NMR ($CDCl_3$) δ 7.61 (s, 1H), 7.52 (s, 1H), 7.33–7.29 (m, overlapped signals, 4H),

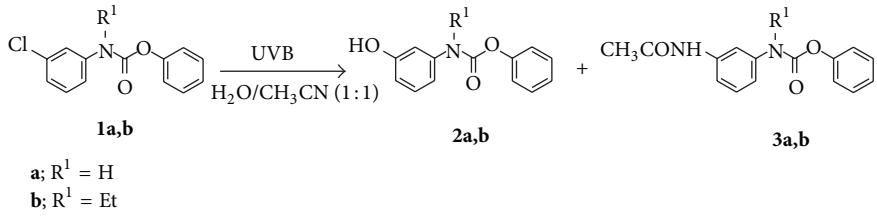


Figure 2: Irradiation of compounds **1a** and **1b**.

7.16 (t, J = 7.1 Hz, 1H), 7.10 (br s, 2H), 7.04 (d, J = 7.2 Hz, 1H), 3.81 (br q, 2H), 2.12 (s, 3H), 1.24 (br t, 3H).

*Phenyl N-4-Acetamidophenyl-N-ethylcarbamate (**3d**)*. mp 156.6–159.0°C (chloroform/methanol); EI-MS m/z 298, 205, 177, 135; UV λ_{max} (H_2O/CH_3CN 1/1) nm 250 (log ε 10.2); ^{1}H NMR (CD_3OD): δ 7.63 (d, J = 9.0 Hz, 4H), 7.34 (br m, 2H), 7.31 (d, J = 9.3 Hz, 2H), 7.20 (br m, 1H), 7.05 (br s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 2.16 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

3. Results and Discussion

Phenyl *meta*-chlorophenyl carbamates **1a**,**b** can be distinguished by the presence of chlorine on the *N*-aryl group (function present in chlorpropham) and by the different substitution on nitrogen (function present in phenisopham) (Figure 2). Irradiation was followed by HPLC and interrupted at a conversion of ca. 20–40%. Compound **1a** was converted for 30% after 2 h. Preparative TLC chromatography led to isolation of unreacted **1a** (71%), hydroxy derivative **2a** (14%), and a product (15%) to which structure **3a** was assigned by spectroscopic means (Figure 2). In particular, mass spectrum of **3a** showed the absence of isotopic chlorine peaks and a peak at 270 m/z indicating the presence of another nitrogen. Moreover, in the proton spectrum a typical singlet at δ 2.16 associated to a methyl linked to a carbonyl group and in the ^{13}C NMR a quaternary low-field signal at δ 168.4 indicated the substitution of chlorine with $NHCOCH_3$ group. The percentages of photoproducts were deduced by integration of selected signals in the proton NMR of the irradiation mixture and confirmed by chromatography.

Similar results were obtained starting from *N*-ethyl derivative **1b** which, however, required a longer irradiation time. After 14 h of irradiation **1b** was 78% in addition to **2b** (10%) and **3b** (12%) (Figure 2).

The different photodegradation rates of **1a** and **1b** could be due to the different intensities of UV absorptions. Indeed, as shown in Figure 3, the *N*-monosubstituted carbamate **1a** exhibits stronger absorption bands than the *N*-ethyl analogue **1b**, even in 280–300 nm range.

Despite the presence of the *O*-aryl moiety, the photoinduced carbamate cleavage was not observed and only dehalogenated products, phenols **2a,b**, and acetamides **3a,b**, were isolated. Photohydrolysis to give phenols is the most frequent photoreaction of halogenated aromatic compounds in water and is reported to occur by a photoionization process, favoured by the medium, [18, 19]. Accordingly, phenols **2a**,**b** should derive from the radical cation **4** that can be trapped by water (pathway **a**, Figure 4) [18, 19]. The attack on the radical cation **4** by nitrogen of acetonitrile and subsequent hydrolysis should give compounds **3a**,**b** (pathway **b**, Figure 4). Compounds **2** and **3** can also be formed by nucleophilic solvent trapping of an aryl cation deriving from homolysis, followed by in-cage electron transfer [18].

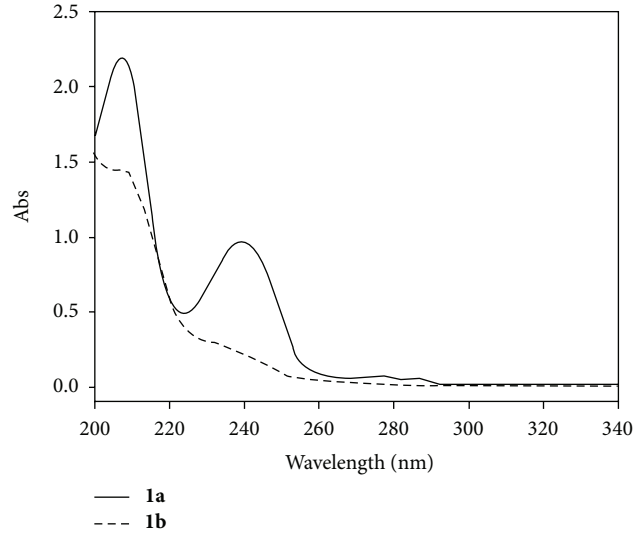


Figure 3: UV-vis spectra of **1a** and **1b** in H_2O/CH_3CN (1 : 1 v/v) (5×10^{-5} M).

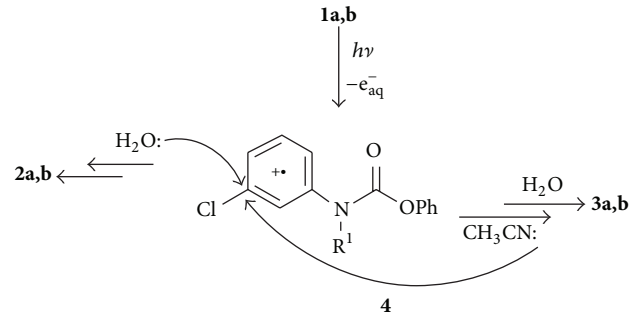


Figure 4: Suggested pathways for photoproducts **2a**,**b**, and **3a**,**b** formation.

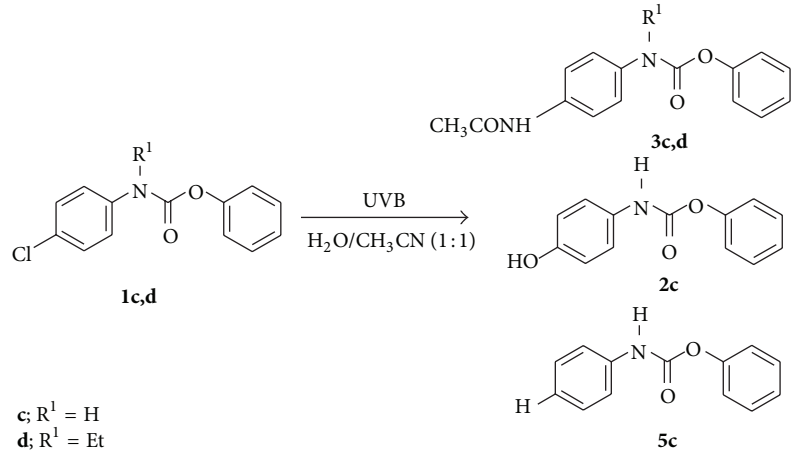


Figure 5: Irradiation of compounds **1c** and **1d**.

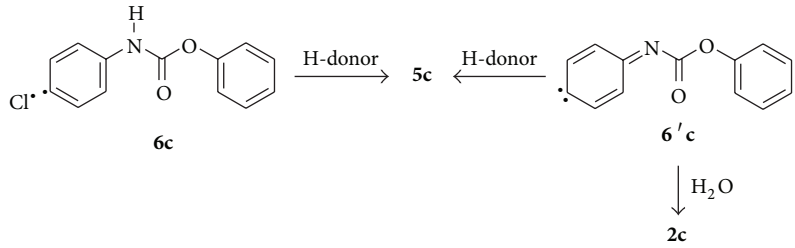


Figure 6: Suggested intermediates for the photoproducts **5c** and **2c**.

Acetamides as **3** have been found by irradiating halogenated compounds [20] or dienes [21] in aqueous acetonitrile, and it has been shown that this solvent is involved in their formation in a so-called photo-Ritter reaction [20, 21]. Control experiments showed that, as expected, the amounts of photo-Ritter products **3a**,**b** decreased with increasing the water content in the reaction medium. For example, amount of **3a** decreased from 15% to 5% when the acetonitrile amount decreased from 50% to 30%. It is interesting to note that the conversion of **1c** is accelerated (30% after only 1 h) by water increase in the reaction medium, because the first photochemical event is the photoionization that is favoured by the aqueous medium.

Halogen-substitution reactions were also observed for *para*-chloroderivatives **1c,d** (Figure 5). After 2 h **1c** was almost completely degraded. However, compounds **2c** and **3c** were recovered in small amounts. The main product was a dechlorinated compound, the diphenyl carbamate **5c** (=**1e**, see Figures 5 and 6), in addition to a significant amount of polymeric material. After 2 h the yields were **1c** (10%), **2c** (8%), **3c** (15%) **5c** (34%), and polymeric material (ca. 33%). As **1b**, *N*-ethyl derivative **1d** was converted slowly and the sole product identified was acetamide **3d** (after 10 h **1d** (71%), **3d** (29%)) (Figure 5).

Photoreduction has been sometimes observed in the irradiation of halogenated aromatic compounds, mainly in *para*-substituted derivatives [18]. A radical mechanism has been proposed so that formation of **5c** should occur probably via intermediate **6c** (Figure 6). It is also plausible that, as suggested in similar cases [19], a carbene intermediate **6′c** is involved in the formation of **5c** and also **2c**, thus justifying the absence of similar compounds for **1d** (Figure 6).

Unsubstituted *N*-aryl compounds **1e** and **1f** exhibited high photostability. After 42 h <5% of **1e** was converted and only hydroxybenzoic acid **7** was identified by HPLC (Figure 7). Differently, from what was observed for the couples **1a**,**b** and **1c**,**d**, *N*-ethyl derivative **1f** appeared more photoreactive than its NH analogue **1e**. Indeed, after the same irradiation time (42 h) it was converted for 24% and chromatography gave **1f** (75%), the acid **7** (18%), the *para*-benzamide **8f** (6%) and the *ortho*-benzamide **9f** (trace) (Figure 7).

Structures **8f** and **9f** derive by a typical photo-Fries rearrangement. As well known [22], this reaction occurs via homolytic cleavage of the carbonyl-heteroatom single bond giving the caged radical pair **10** (Figure 8). In-cage recombination in *para* and/or *ortho*-position affords the acyl migration products as **8f** and **9f**, respectively.

para-Hydroxybenzoic acid **7** could be formed by hydrolysis of **8** due to the long water contact for the prolonged irradiation. Stabilization of radicals by substitution could account for the breakage less difficult in *N*-ethyl compound **1f** than **1e**.

4. Conclusions

Our results show that the *N*-aryl *O*-aryl substitution is not a sufficient condition to have a photo-induced breaking of

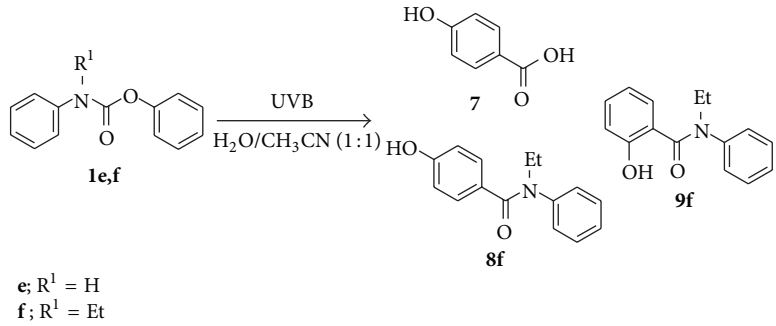


Figure 7: Irradiation of compounds **1e** and **1f**.

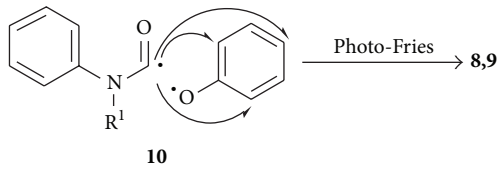


Figure 8: Suggested pathways for the photoproducts **8** and **9** formation.

the carbamate bond. This process is completely overcome in the presence of other photosensitive functions as chlorine on the *N*-aryl ring. In the latter case photosolvolysis or photoreduction occurs depending on the halogen position on the ring.

The *N*-substitution does not affect the product formation but influences the degradation rate due to radical stabilization or to a lower absorption of UVB radiation.

An interesting result is the obtaining of the photo-Ritter products derived from the nucleophilic trapping of radical cations by acetonitrile. We proved that when the pesticide chlorpropham was irradiated in H_2O/acetonitrile 1 : 1 v/v, a product with similar spectroscopic data as **3c**,**d** was formed.

Acetonitrile is generally used in environmental investigation as cosolvent to have clear aqueous solutions of compounds slightly soluble in water. The U.S. Environmental Protection Agency in the Fate and Transformation of chemicals Test Guidelines [23] suggests that the use of acetonitrile should be preferably not exceeding 1%, but cosolvent percentages up to 10% are allowed. Hence, to avoid mistakes, characterization of photoproducts is necessary.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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[23] Spectroscopic data of *isopropyl N-3-acetamidophenylcarbamate*: EI-MS *m/z* 236, 194, 177, 152, 108; UV λ_{max} (H_2O/CH_3CN 1:1 v/v) 225 nm (log 3.7), 280 nm (log 2.7); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.23 (d, J = 7.1 Hz, 2H), 7.15 (br s, 1H), 7.11 (m, 1H), 6.56 (br s, 1H), 5.00 (sept, J = 6.3 Hz, 1H), 2.16 (s, 3H), 1.30 (d, J = 6.2 Hz, 6H).