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# On the Photochemical Reactivity of Phthalonimide

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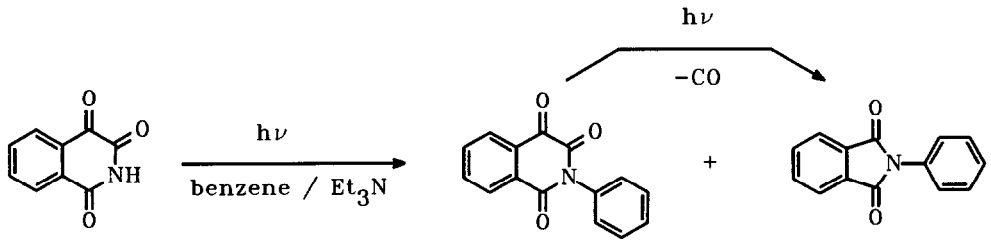
**Abstract:** The occurrence of an electrophilic phthalonimidyl radical is proposed to account for the N-arylation products obtained by irradiation of phthalonimide in benzene in the presence of an amine and oxygen. Normal carbonyl reactivity is observed in the photochemical reactions of phthalonimide with furan (oxetane formation) and hydrogen donors (photoreduction).

## INTRODUCTION

The photochemistry of compounds possessing the imide functionality includes a variety of reactions, such as most known carbonyl processes, as well as some unparalleled reactions[1]. Special attention has been paid to the photochemical behaviour of phthalimide-related aromatic imides[2] and their synthetic uses[3]. These compounds take part in additions and reductions[4], hydrogen abstraction[5], intramolecular cyclizations[6] and reactions with alkenes, whether by insertion into a C-N bond[7], cycloaddition to an aromatic ring[8], oxetane formation[9] or addition with incorporation of solvent[10]. Notwithstanding the potentially interesting photochemistry to be expected from its high functionality the phthalonimide system has not yet been studied in this respect. Some related systems such as acyclic α-oxoimides[11] and cyclic and acyclic α-oxoamides[12,13] have attracted much attention on the grounds of their potential synthetic use. Also, the cyclic analogs *N,N'*-dialkylpiperazintetrones[14] and imidazolidinetriones exhibit interesting inter- and intra-molecular photoreactivity[15]. Our exploratory study of the photochemistry of phthalonimide was initially focused on the photoreduction of the molecule as a means of elucidating the reactivity of its carbonyl groups. The results obtained are reported alongside a new, unexpected N-arylation process observed.

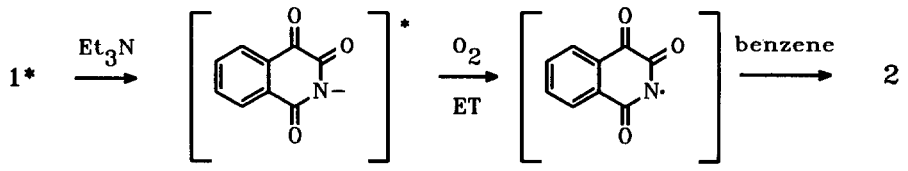
## RESULTS AND DISCUSSION

The photoreactivity of the ketone carbonyl in **1**, as a part of an α-oxoimide particularly the possibility of a twofold reduction to homophthalimide as in diaryl-pirroline-4,5-diones (isatin type derivatives)[12], was initially investigated. Under analogous experimental conditions, benzene was used as solvent and triethylamine as reductant. The solution was purged with argon before irradiation, and the reaction was monitored by GC/MS and allowed to proceed to a high conversion. Chromatographic separation of the reaction products afforded a major component which analyzed for $C_{15}H_9NO_3$. Incorporation of a six-carbon atom fragment was also evident from $M^+$ at m/z 251 in the EI-MS. The $^{13}$C-NMR spectrum showed three carbonyl signals and the absence of the N-H proton in the $^1$H-NMR was suggestive of an *N*-phenyl phthalonimide (**2**) structure. The second compound isolated was readily identified as *N*-phenyl phthalimide (**3**) from the symmetry of the signals observed in both the $^1$H- and the $^{13}$C-NMR spectrum. Independent syntheses of **2** and **3** further confirmed both structures.




1 2 3

In order to account for the N-arylation process leading to **2** and **3**, several experiments were carried out. Irradiation in deuterated benzene afforded *N*-(phenyl-$d_5$) phthalonimide (m/z 256) and *N*-(phenyl-$d_5$) phthalimide (m/z 228), thus confirming the origin of the phenyl group. No reaction took place when irradiation was applied in the absence of amine. Because the C-N bond formation implies an oxidation process, some oxygen was needed, so the reaction was quite inefficient under strictly deoxygenated conditions. Bearing these facts in mind, the formation of **2** can be explained by assuming the production of an imidyl radical that is electrophilic enough to add to benzene[16]. A similar behavior was observed for the phthalimidyl radical resulting from the photochemical ß-cleavage of the weak N-O bond of *N*-tosyloxyphthalimide[17]. Because **1** lacks such a weak bond the imidyl radical may result from deprotonation of the excited phthalonimide by the amine to give the excited phthalimidate anion followed by an electron transfer to molecular oxygen (Scheme I).

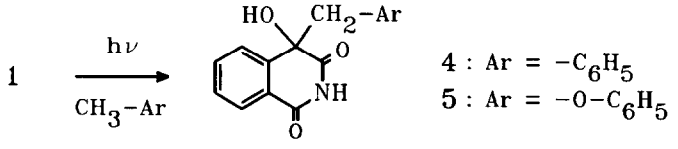


Scheme I

Involvement of the excited anion of **1** was supported by the following facts: phthalonimide in benzene does no fluoresce, and its absorption spectrum is not affected by the addition of $NEt_3$ (this solution exhibits a strong fluorescence band at 517 nm on excitation at 382 nm). That this emission might be related to the presence of the imidic N-H bond and the action of the amine was inferred from the fact that N-methyl phthalonimide did not fluoresce under any conditions, thus excluding the possibility of charge transfer complex emission[18].

Irradiation of **2** under the same experimental conditions afforded **3** as the main product, thereby showing that **3** was not a primary product in the photoreaction of phthalonimide. Its decarbonylation can be a result of a twofold α-cleavage, a process already observed in the photochemistry of *N,N'*-dimethyl-piperazinetetrone[19].

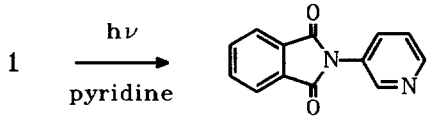
Increasing the nucleophilicity of the aromatic system by using toluene or anisole should have resulted in faster N-arylation. However, irradiation of a toluene solution of **1** and $NEt_3$ afforded the photoadduct **4** in a high yield. The presence of the N-H and H-5 signals upfield in the $^1$H-NMR spectrum indicated that the reaction took place at C-4. With anisole as solvent, the reaction proceeded identically and afforded the photoadduct **5**. The reaction was not affected by the concentration of $NEt_3$ over the range from 0 to 0.32M.



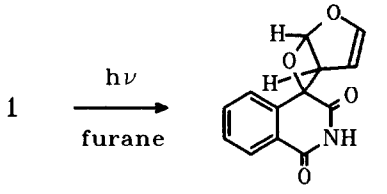
Next, we assayed the photoreaction in pyridine as solvent, in the confidence that it would provide the basicity and nucleophilicity required to produce and trap the phthalonimidyl radical. A slow, complex reaction resulted and a single compound **6** was isolated in a low yield (32%). The EI-MS showed an even molecular ion (m/z 224) reflecting pyridine incorporation and consistent with an N-substituted phthalimide structure. That the substitution took place at the 3-position of the pyridine can readily be inferred from the two down field aromatic protons (H-2' and H-6') observed in the $^1$H-NMR spectrum,

one of them showing the absence of the expected *ortho* coupling constant. The structure was confirmed by independent synthesis of **6**. Based on these results, **6** was assumed to be formed by decarbonylation of the primary product, *viz.* the N-(3'-pyridyl) phthalonimide. Radical substitution reactions of pyridine occur preferentially at position 2, however for much more electrophilic attacking radicals position 3 is more favorable[20]. Owing to the complexity of the reaction mixture, the formation of other isomers cannot be excluded.

The low reactivity of pyridine, prompted us to use a $\pi$-excedent heterocycle such as furan, which is known to be selectively attacked by radicals at position 2 (it is almost 12 times more reactive than benzene[21]). Irradiation of **1** in the presence of triethylamine and furan as solvent afforded a single product **7**, as showed by tlc, though isolated in a low yield. That the reaction took a different way was obvious from the presence of only two carbonyl groups in the $^{13}$C-NMR spectrum. The absence of a molecular ion in the EI-MS (furan loss) and two coupled vinyl protons in the $^{1}$H-NMR spectrum, point to the oxetane




6

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structure. Involvement of the carbonyl group at C-4 was inferred from the down field chemical shift for H-5. Spectroscopic data were consistent with a 2,7-dioxabicyclo[3,2,0]-hept-3-ene substructure resulting from the wellknown regio- and stereo-selective photocycloaddition of furan to carbonyls[22]. The *exo* position of the bicyclic system was occupied by the aromatic ring as inferred from the chemical shift for the bridgehead proton 5'[23]. As expected for the photochemical formation of oxetane, the reaction proceeded identically in the absence of the amine.

These results suggest that, in the presence of hydrogen donors or double bonds, the carbonyl group at C-4 in excited phthalonimide behaves as a normal n-$\pi^*$ triplet state carbonyl[22,24]. In the absence

of hydrogen donors and double bonds, an electrophilic phthalonimidyl radical capable of adding itself to aromatic substrates may be produced. The experimental result support the involvement of an amine and oxygen in this process. Whether this behaviour is specific to phthalonimide or shared by other cyclic imides is been currently investigated in our laboratory.

## EXPERIMENTAL

*General.* Melting points are uncorrected. Ir spectra (KBr) were recorded on a Perkin-Elmer IR-883 spectrophotometer. $^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker WP-200 SY spectrometer. Chemical shift data are given in ppm and referred to internal TMS. Mass spectra (70 eV, direct insertion) were obtained on a Hewlet-Packard 5988A instrument equipped with electron impact ionization. Fluorescence measurements were made on a Perkin-Elmer LS-5 luminescence spectrometer. Elemental analyses were performed at the CHN Service of the University of Málaga, Spain. Preparative irradiations were conducted by using a 125 W medium-pressure mercury lamp (General Electric H125/27) in a Pyrex immersion well reactor at near-room temperature. Prior irradiation, solutions were bubbled with argon for 10 min. Phthalonimide and N-methyl phthalonimide were prepared by oxidation of the corresponding isocarbostyril with sodium dichromate[25]. Isocarbostyril was obtained by photolysis of isoquinoline N-oxide in methanol[26].

**Irradiation of phthalonimide (1) in benzene:** A solution of **1** (1 mmol) and triethylamine (3 mmol) in benzene (150 ml) was irradiated at near room temperature. The reaction was monitored by GC/MS and allowed to proceed to *ca.* 90% conversion (4 h). The solvent was then removed *in vacuo* and the residue column chromatographed over silica gel (eluent: 2:3, AcOEt/hexane). Further purification by tlc yielded **1** (18 mg, 10%), **2** (114 mg, 45%) and **3** (79 mg, 35%).

**N-phenyl phthalonimide (2)**: mp 203-205 °C (benzene) (lit.,[27] mp 218.5 °C). $^1$H-NMR ($CDCl_3$) $\delta$ 8.23 (m, 2H, H-5 and H-8), 7.80 (m, 2H, H-6 and H-7), 7.41(m, 3H, H-2', H-4' and H-6') and 7.13 (m, 2H, H-3' and H-5'). $^{13}$C-NMR ($CDCl_3$) $\delta$ 174.7 (C-4), 162.2 (C-3), 156.8 (C-1), 136.1 (C-7), 134.6 (C-6), 133.7 (C-1'), 131.1 (C-4a), 130.1 (C-8), 129.9 (C-8a), 129.4 (C-3' and C-5'), 129.2 (C-4'), 128.1 (C-2' and C-6') and 127.9 (C-5). IR($\nu$, $cm^{-1}$) 1734, 1688, 1593. EI-MS, m/z(%) 251 ($M^+$, 15), 223 (37), 179 (61), 104 (87), 76 (100). Anal. Calcd. for $C_{15}H_9NO_3$: C, 71.71; H, 3.61; N, 5.57. Found: C, 71.89; H, 3.75; N, 5.21.

**N-phenyl phthalimide (3)**: mp 198-200 °C (EtOH) (lit.,[28] 205-206°C). $^{13}$C-NMR($CDCl_3$) $\delta$ 162.7, 134.3, 131.8, 129.0, 128.0, 126.5 and 123.7. EI-MS, m/z(%) 223 ($M^+$, 40), 179 (100), 76 (88).

**Irradiation of phthalonimide (1) in toluene**: A solution of **1** (1 mmol) in toluene (150 ml) was irradiated for 1 h. After removal of the solvent, the reaction mixture was purified by column chromatography (silica gel, eluent: $CHCl_3$) to give **4** (240 mg, 90 %).

**1,3(*2H,4H*)-4-benzyl-4-hydroxy isoquinolinedione (4)**: mp 139-41 °C (AcOEt-hexane). $^1$H-NMR ($CDCl_3$) $\delta$ 8.98 (bs, 1H, NH), 8.02 (d, 1H, J=7.5Hz, H-8), 7.68 (m, 2H, H-6 and H-5), 7.48 (m, 1H, H-7), 7.12 (m, 3H, H-2',H-4' and H-6'), 6.70 (m, 2H, H-3' and H-5'), 4.20 (bs, 1H, OH), 3.23 (d, 1H, J=12.8Hz, H$\alpha$) and 3.14 (d, 1H, J=12.8Hz, H$\alpha$'). $^{13}$C-NMR ($CDCl_3$) $\delta$ 175.3(C-3), 163.0(C-1), 140.9(C-4a), 134.4(C-6), 133.1(C-1'), 130.1(C-2' and C-6'), 128.6 (C-8), 128.2 (C-3' and C-5'), 127.9 (C-7), 127.7 (C-5), 126.0 (C-4'), 124.4 (C-8a), 76.3 (C-4) and 53,5 (C$\alpha$). Ir($\nu$, $cm^{-1}$) 3320, 1691, 1605. EI-MS, m/z(%) 267 ($M^+$, 3), 176 (32), 149 (35), 104 (8), 91 (100). Anal. Calcd. for $C_{16}$ $H_{13}$ N $O_3$: C, 71.91; N, 4.87; H, 5.24. Found: C, 71.72; N, 4.85; H, 5.38.

**Irradiation of phthalonimide (1) in anisole**: A solution of **1** (1 mmol) in anisole was irradiated (3 h) to almost complete disappearance of the starting material (tlc). Vacuum distillation of the solvent left a residue that was column chromatographed (silica gel, eluent: 1:4, AcOEt/hexane) to obtain **5** (238 mg, 85%).

**1,3(*2H,4H*)-4-hydroxy-4-phenoxymethyl isoquinolinedione (5)**: mp 159-161 °C ($CCl_4$). $^1$H-NMR ($CDCl_3$) $\delta$ 8.70 (bs, 1H, NH), 8.18 (dd, 1H, J=7.7 and 1.5Hz, H-8), 7.79 (dd, 1H, J=7.7 and 1.5Hz, H-5), 7.71 (dt, 1H, J=7.7, 7.7 and 1.5Hz, H-6), 7.53 (dt, 1H, J=7.7, 7.7 and 1.5Hz, H-7), 7.12 (m, 2H, H-2' and H-6'), 6.90 (m, 1H, H-4'), 6.69 (m, 2H, H-3' and H-5'), 4.05 (bs, 1H, OH), 4.20 (d, 1H, J=8.6Hz, H$\alpha$) and 4.01 (d, 1H, J=8.6Hz, H$\alpha$'). $^{13}$C-NMR ($Cl_3CD$) $\delta$ 174.2 (C-3), 163.6 (C-1), 157.7 (C-1'), 138.8 (C-4a), 134.6 (C-6), 129.5 (C-3' and C-5'), 129.1 (C-8), 128.2 (C-7), 125.5 (C-5 and C-8a), 122.0 (C-4'), 114.8 (C-2' and C-6'), 76.7 (C$\alpha$) and 74.3 (C-4). IR($\nu$, $cm^{-1}$) 3380, 1696, 1597. EI-MS, m/z(%) 283 ($M^+$, 7), 149 (9), 107 (100), 77(45). Anal. Calcd. for $C_{16}H_{13}NO_4$: C, 67.84; N, 4.63; H, 4.94. Found: C, 67.85; N, 4.69; H, 4.70.

**Irradiation of phthalonimide (1) in pyridine**: A pyridine (150 ml) solution of **1** (1 mmol) was irradiated for 8 h. The pyridine was then removed *in vacuo* and the reaction mixture was separated by column chromatography over silica gel (eluent: 2:3, AcOEt/hexane) to afford **1** (32 mg, 18%) and **6** (72 mg, 32%).

**N-(3'-pyridyl) phthalimide (6)**: mp 167-168 °C (EtOH) (lit.,[29] 170-171 °C). $^1$H-NMR ($CDCl_3$) $\delta$ 8.72 (dd, 1H, J=2.3 and 0.6Hz, H-2'), 8.69 (dd, 1H, J=4.9 and 1.5Hz, H-6'), 7.93 (m, 2H, H-4 and H-7), 7.78 (m, 3H, H-5, H-6 and H-4') and 7.40 (ddd, 1H, J=8.2, 4.9 and 0.6Hz, H-5'). $^{13}$C-NMR ($CDCl_3$) $\delta$ 166.6 (C-1 and C-3), 148.7, 147.2 (C-2'and C-6'), 134.6 (C-5 and C-6), 133.6 (C-4'), 131.6 (C-3a and C-7a), 128.9 (C-3'), 123.9 (C-4 and C-7) and 123.5 (C-5'). IR ($\nu$, $cm^{-1}$) 1736, 1703, 1482. EI-MS, m/z(%) 224 ($M^+$, 100), 180 (31), 104 (24), 76(46). Anal. Calcd. for $C_{13}H_8N_2O_2$: C, 69.64; N, 3.60; H, 12.49. Found: C, 69.36; N, 3.47; H, 12.44.

**Irradiation of phathalonimide (1) in furan**: A solution of **1** (1 mmol) in dry and freshly distilled furane (150 ml) was irradiated, the reaction being monitored by tlc. After 8 h, furan was removed by distillation

and the residue column chromatographed (silica gel, eluent: 2:3, AcOEt/hexane) to afford **1** (22 mg, 13 %) and **7** (99 mg, 38%).

**1,3(*2H,4H*)-isoquinolinedione-4-spiro-6'-2',7'-dioxabicyclo[3,2,0]-hept-3'-ene (7)**: mp 190-192 °C (EtOH). $^1$H-NMR ($CDCl_3$:$CD_3OD$) $\delta$ 8.08 (dd, 1H, J=7.7 and 1.4Hz, H-8), 7.84 (dd, 1H, J=7.7 and 1.4Hz, H-5), 7.67 (dt, 1H, J=7.7, 7.7 and 1.4Hz, H-6), 7.45 (dt, 1H, J=7.7, 7.7 and 1.4 Hz, H-7), 6.68 (ddd, 1H, J=2.9, 1.2 and 0.7Hz, H-3'), 6.65 (dd, 1H, J=4.2 and 0.7Hz, H-1'), 4.50 (t, 1H, J=2.9 and 2.9Hz, H-4') and 4.17 (ddd, 1H, J=4.2, 2.9Hz and 1.2Hz, H-5'). $^{13}$C-NMR ($CDCl_3$:$CD_3OD$) $\delta$ 174.1 (C-3), 163.8 (C-1), 151.2 (C-3'), 138.8 (C-4a), 134.7 (C-6), 129.0 (C-8), 128.4 (C-7), 126.6 (C-5 and C-8a), 108.3 (C-1'), 105.6 (C-4'), 74.5 (C-4) and 47.2 (C-5'). IR($\nu$, $cm^{-1}$) 3421, 1699, 1605. EI-MS, m/z(%) 175 ($M^+$-$C_4H_4O$, 36), 147 (65), 132 (21), 104(100), 81(70), 76(84). Anal. Calcd. for $C_{13}H_9NO_4$: C, 64.20; N, 3.70; H, 5.76. Found: C, 64.05; N, 3.64; H, 5.55.

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