

# Photoinduced Molecular Rearrangements. The Photochemistry of Some 1,2,4-Oxadiazoles in the Presence of Nitrogen Nucleophiles. Formation of 1,2,4-Triazoles, Indazoles, and Benzimidazoles

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The photochemistry of some 3,5-disubstituted 1,2,4-oxadiazoles in the presence of nitrogen nucleophiles [*external*, such as added amines or hydrazines, or *internal*, such as an *o*-aminophenyl moiety at C(3) of the oxadiazole ring] has been investigated. In the irradiation of 5-amino-(or 5-*N*-substituted amino) 3-phenyl-1,2,4-oxadiazoles in the presence of aliphatic primary amines (or ammonia), photolytic species arising from heterolytic cleavage of the ring O–N bond capture the nucleophilic reagent to give open-chain intermediates, which develop into 1,2,4-triazolin-5-ones. Similarly, irradiations of 3,5-diphenyl-, 3-methoxy-5-phenyl-, and 5-methyl-3-phenyl-1,2,4-oxadiazoles gave 1,2,4-triazoles. In the same context, irradiations of representative substrates in the presence of hydrazines have been also investigated. In the irradiation of 3-(*o*-aminophenyl)-5-methyl-, 3-[*o*-(methylamino)phenyl]-5-methyl-, and 3-(*o*-aminophenyl)-5-phenyl-1,2,4-oxadiazoles, concomitant formation of indazoles and benzimidazoles, presumably arising from a common photolytic species, has been observed. Some mechanistic aspects have been considered, and possible applications in synthesis have been pointed out.

## Introduction

The photochemistry of 3,5-disubstituted 1,2,4-oxadiazoles in methanol is characterized by photolysis of the ring O–N bond into open-chain species which develop into final products depending on the nature and position of substituents.<sup>1–8</sup> A quite generalizable behavior was recognized in the formation of compounds arising from a reaction of the electrophilic nitrogen of the photolytic species with the nucleophilic solvent.<sup>1b,3</sup> In some cases, nitrene-type intermediates can even isomerize into a carbodiimide which the solvent will then capture.<sup>3,8</sup> Moreover, in the irradiation of 5-aryl substituted oxadiazoles, the formation of quinazolinones has been reported and explained by a heterocyclization reaction involving the electrophilic nitrogen of the photolytic species and the C(5)-aryl moiety.<sup>1b,3,7</sup> Furthermore, photoinduced rearrangements of oxadiazoles containing certain three-(four-)atom side-chains linked at C(3) have been also recognized.<sup>4–6</sup>

In pursuing our interest<sup>8–11</sup> in the photochemistry of five-membered heterocycles both from a mechanistic and

a synthetic point of view, and to get more insight in the photochemistry of 1,2,4-oxadiazoles, we now planned to study irradiations of variously substituted substrates in the presence of nitrogen nucleophiles. This would have allowed us to extend the understanding of the photolysis of these systems and to open up some novel synthetic transformations. For the study we have at first considered irradiations of oxadiazoles **1–3** and **13–15** in the presence of an *external* nucleophile such as an added amine or hydrazine. Significantly, compounds **1–3** are characterized by a substituent at C(5) having a conjugative electronic effect in one hand and a possible leaving-group ability in the other. Furthermore, we have considered compounds **27–29** containing an *o*-aminophenyl group at C(3) of the oxadiazole ring: interestingly, this group had to be considered an *internal* nitrogen nucleophile, which would have been well arranged for a heterocyclization reaction involving any ring-photolytic species. In their turn, oxadiazoles **27**, **28**, and **29** are known<sup>12</sup> to rearrange thermally into 3-(acylamino)indazoles **32**, **33**, and **34**, respectively, following the Boulton/Katritzky rearrangement pattern.<sup>13</sup> In particular, owing to the low nucleophilic character of the attacking nitrogen, these rearrangements take place under severe conditions.<sup>12</sup>

## Results and Discussion

**Irradiations of 5-Amino-(or 5-*N*-substituted amino)-3-phenyl-1,2,4-oxadiazoles.** We have considered irradiations (at  $\lambda = 254$  nm in methanol) in the

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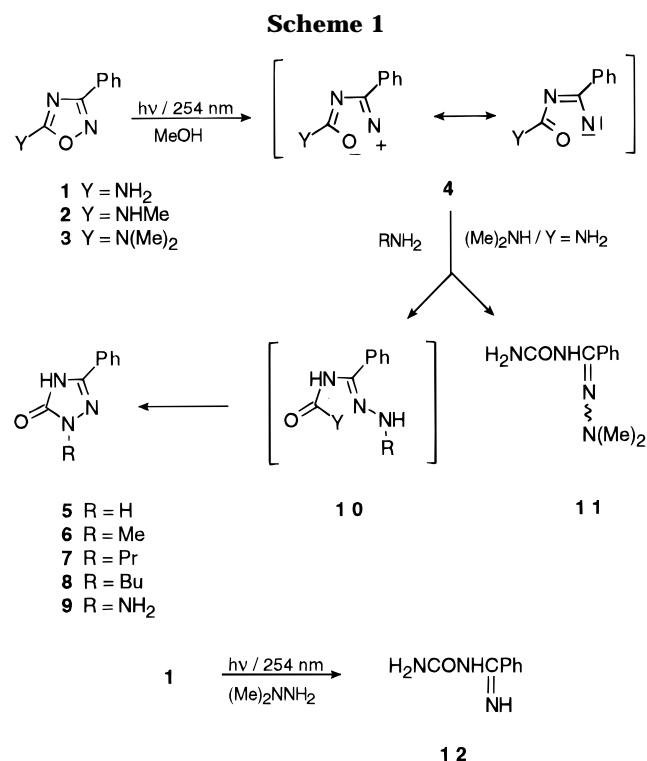
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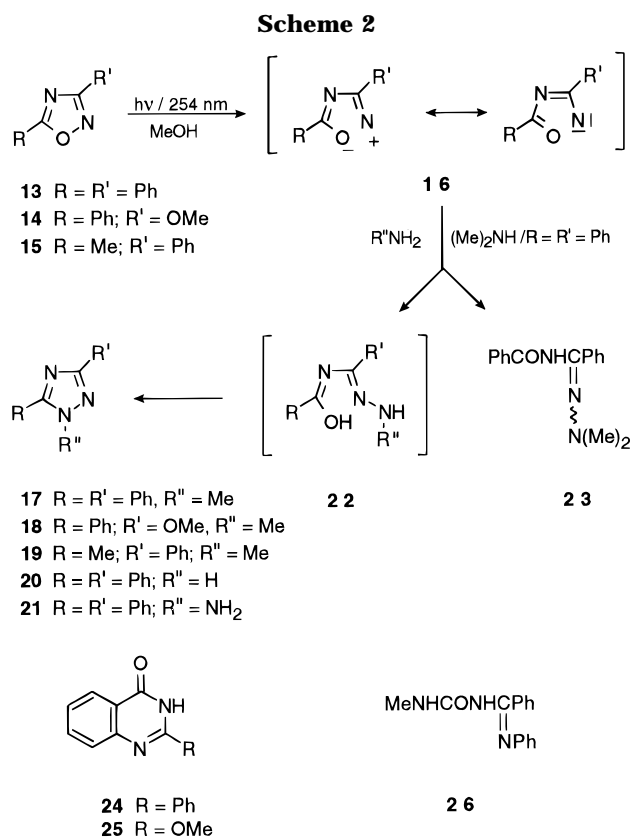
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presence of primary aliphatic amines such as methylamine. In some instances, for demonstrative purposes, methanolic ammonia, propylamine, or butylamine was also employed. Moreover, irradiations in the presence of hydrazine have been representatively tested. In any case, by means of parallel reactions, we have ascertained that starting substrates were inert under thermal aminolysis or ammonolysis conditions.

Irradiation of oxadiazoles 1–3 in the presence of an excess of ethanolic methylamine produced the 1-methyl substituted 1,2,4-triazolin-5-one 6. Similarly, when irradiated in the presence of methanolic ammonia, propylamine, or butylamine, compound 1 gave the unsubstituted triazole 5 or the 1-alkyl substituted compounds 7 and 8, respectively. Because of the occurrence of minor photoreactions and/or secondary processes, yields of isolated products were not improved more than 60%. Significantly, in the irradiation of the oxadiazole 1 in the presence of methanolic ammonia, some amounts of the carbamoylbenzamidine 12 have been also detected (see later on). Furthermore, parallel irradiations of the representative oxadiazole 1 in methanol with and without methylamine showed (by HPLC; at low conversion of starting material) that the rate of disappearance of starting material was not affected by the presence of the amine.

These results may be accommodated by assuming a reaction of the photolytic species 4 with the actual nucleophile to give open-chain intermediates 10 (Scheme 1). Subsequent selective cyclization of 10 into 1,2,4-triazolin-5-ones will then imply elimination of the YH moiety. Accordingly, irradiation of 1 in the presence of dimethylamine gave 11. The formation of an N–N bond in the reaction between 4 and an *external* nitrogen-nucleophile appears noteworthy, especially when mechanistic and synthetic aspects of these photoreactions are considered. By contrast, *internal* N–N bond-formation by direct cyclization of (4; Y = NH<sub>2</sub> or NHMe) into the triazole nucleus does not occur.<sup>3</sup>



To obtain 1-amino-1,2,4-triazolin-5-ones, we have then irradiated the representative oxadiazole 1 in the presence of hydrazine monohydrate. As expected, the photoreaction gave the 1-amino compound 9, but fair yields were observed because, *inter alia*, some amounts of the photochemically deaminated compound 5 were also formed. This photoreactivity, however, did not appear applicable to the use of alkylhydrazines. For example, irradiation of 1 in the presence of *N,N*-dimethylhydrazine failed to give the expected 1-(*N,N*-dimethylamino)triazolin-5-one derivative; surprisingly, this photoreaction mainly gave the carbamoylbenzamidine 12, as a result of a redox reaction. Although abstraction of hydrogens by the ring-photolytic species is documented in the photochemistry of 1,2,4-oxadiazoles,<sup>1,8</sup> further investigations regarding the role of the hydrogen-donor reagent appear to be necessary. In the present case, the reduction may proceed by the usual intermediate [10; R = N(Me)<sub>2</sub>] which will collapse by electron flow from nitrogen of the hydrazine moiety into the imine nitrogen atom,<sup>14</sup> rather than by cyclization into the triazole ring.

**Irradiations of 3-Phenyl-(or 3-methoxy)-5-substituted-1,2,4-oxadiazoles.** Irradiation of compounds 13, 14, and 15 in the presence of methylamine gave triazoles 17, 18, and 19, respectively, through intermediates 22 (Scheme 2). Accordingly, irradiation of 13 in the presence of dimethylamine gave compound 23. Similarly, irradiation of 13 in the presence of methanolic ammonia or hydrazine gave 20 or 21, respectively.

On the whole, irradiations of oxadiazoles 13–16 proceeded with lower conversion of starting material, and then lower yields of final triazoles were found. On the other hand, increasing irradiation time did not significantly increase yields of triazoles (after prolonged ir-

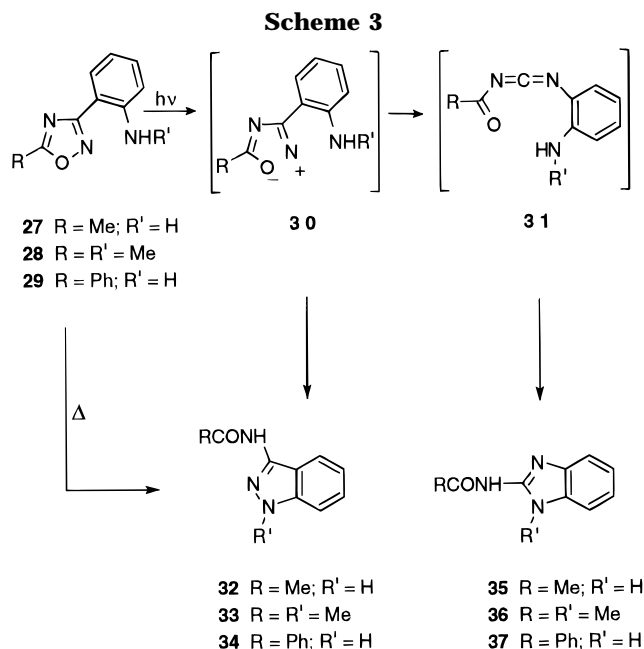
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radiations, they did not exceed values of about 30% because secondary processes also take place. In the irradiation of 5-phenyl substituted oxadiazoles **13** and **14** we also isolated some amounts of the quinazolin-4-ones **24** and **25**, respectively, which originate from a heterocyclization reaction involving the C(5)-phenyl ring. (Further investigations are necessary to clarify the role of methylamine, if any, in this concomitant photoreaction). In addition, in the irradiation of the oxadiazole **13** in the presence of methylamine, the *N*-[(methylamino)carbonyl]-*N*-phenylbenzimidine **26**<sup>15</sup> was also found. Furthermore, irradiation of **13** in the presence of *N,N*-dimethylhydrazine mainly gave the *N*-benzoylbenzamide as a reduction product.

The formation of 1,2,4-triazoles from 1,2,4-oxadiazoles deserves some comments. It is well known<sup>16</sup> that 3,5-disubstituted 1,2,4-oxadiazoles show remarkable stability toward hydrolytic reagents [only for oxadiazoles monosubstituted at C(5) or at C(3) is this inertness lost]. Our photochemical results, at least formally, could represent aminolysis (or ammonolysis) at the ring O–N bond, allowing the synthesis of 1,2,4-triazoles. In this context, if one considers the easy workup procedure and the high conversion of starting material, the photoinduced aminolysis of 5-amino-3-aryl-1,2,4-oxadiazoles could be successfully exploited for the synthesis of target 1-alkyl-3-aryl-1,2,4-triazolin-5-ones. On the other hand, despite the low yields of 1-alkyl-3,5-disubstituted 1,2,4-triazoles, this design in synthesis could be of some interest in view of the fact that many 1-substituted 1,2,4-triazoles have found use for their biological activity.<sup>17</sup>

**Irradiations of 3-(*o*-Aminophenyl)- or 3-[*o*-(Methylamino)phenyl]- 5-substituted 1,2,4-Oxadiazoles.** When irradiated at  $\lambda = 310$  nm in methanol, compounds **27** and **28** gave complete conversion of starting material in a rather clean and very fast photoreaction, which produces mixtures of 3-(acetylamino)indazoles [**32** (25%) and **33** (30%)] and 2-(acetylamino)benzimidazoles [**35** (75%) and **36** (70%)], respectively. Irradiation at  $\lambda = 254$  nm produced similar results; however, at this wavelength photoreactions did not follow a clean course, and lower yields have been observed because of the subsequent photoreactivity of final products. Both indazoles and benzimidazoles must be considered primary photoproducts: in fact, separate irradiations (at  $\lambda = 310$  nm) of **32** and **35** (or **33** and **36**) did not show any photochemical interconversion (Scheme 3).

Differently from what was observed for compounds **27** and **28**, irradiation of the 5-phenyl substituted oxadiazole **29** at  $\lambda = 310$  nm proceeded with lower conversion of starting material. Better results have been, however, obtained on irradiating **29** at  $\lambda = 254$  nm: at this wavelength, the conversion was complete and only the expected mixture of the indazole **34** (45%) and benzimidazole **37** (55%) resulted. Moreover, in all cases we



studied, quenching and sensitization experiments gave negative results, showing that singlet excited states are involved.

The concomitant formation of indazoles and benzimidazoles could arise from a common photolytic species **30**. In one hand, this will develop into indazoles through the N–N bond closure, that is, in a manner similar to that observed in the irradiation of previous substrates in the presence of an added amine. In the other, the photolytic species will develop into the carbodiimide **31**, a reasonable precursor of the benzimidazole nucleus. The low nucleophilic character of the attacking amino group appears unfavorable to the indazole ring-closure; by contrast, the migration of the phenyl moiety into **31** could result in an *o*-amino-assisted process. Taking into account that 1,2,4-oxadiazoles can be considered masked *O*-acylamidoximes, we see that photoinduced formation of the benzimidazole ring from 3-(*o*-aminophenyl)oxadiazoles parallels the thermally-induced transformation (in neutral medium) of *o*-amino- (or ortho-*N*-substituted-amino) *O*-acylbenzamidoximes into 2-aminobenzimidazoles.<sup>18</sup> Interestingly, when applied to various 3-(2-aminoheteroaryl)-5-substituted 1,2,4-oxadiazoles, the observed rearrangement could be fruitfully exploited for the synthesis of target benzimidazole hetero analogues.

To gain information on the photoreaction, we irradiated representative **27** in the presence of methylamine as an external nitrogen nucleophile. Taking into account irradiations of previous substrates in the presence of amines, we could have expected to some extent a competitive involvement of the added methylamine. However, parallel irradiations (at  $\lambda = 310$  nm) of the oxadiazole **27** in methanol, with and without methylamine, did not show any difference both in the rate of the conversion of starting material and in the composition of the final photolysate. Compounds **28** (at  $\lambda = 310$  nm) and **29** (at  $\lambda = 254$  nm) behaved similarly. Although an intramolecular heterocyclization should be easier than an intermolecular reaction involving the external reagent, the observed results suggest that the *o*-aminophenyl

(15) A tautomer of **26** could be also considered. Although we have no mechanistic evidence, tentatively the formation of compound **26** (which is independent from the presence of products **17** or **24**) could be explained by assuming the *N*-benzoyl-*N*-phenylcarbodiimide as a reasonable photolytic intermediate. However, whether the migration of the phenyl moiety of the benzoyl group at the carbodiimidic carbon atom will precede or follow the involvement of methylamine remains questionable.

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**Table 1. Energies Values (kJ/mol) of Singlet ( $E_s$ ) and Triplet ( $E_t$ ) State for Compounds 1–3, 13–15, and 27–29 As Determined from Emission Spectra**

compd	$E_s$	$E_t$
<b>1</b>	435	299
<b>2</b>	427	299
<b>3</b>	435	315
<b>13</b>	405	281
<b>14</b>	412	291
<b>15</b>	427	295
<b>27</b>	332	285
<b>28</b>	323	278
<b>29</b>	315	278

chromophore should be involved in an excited state allowing some concertedness in the O–N bond cleavage on one hand, and N–N bond formation (to indazoles) or phenyl migration and ring-closure (to benzimidazoles) on the other.

As last comment, these investigations show that in the photochemistry of 1,2,4-oxadiazoles the first step of the reaction should be considered the breaking of the ring O–N bond; the fate of the intermediate will then depend on the presence of a nucleophile, *internal* or *external* to the reacting molecule, as well as from the possibility of a subsequent heterocyclization reaction. This last behavior adds to the attractiveness of the photochemistry of O–N bond-containing azoles the opportunity of a number of applications in heterocyclic synthesis.

## Experimental Section

**Materials and Methods.** For instruments and general procedures see our previous papers.<sup>9,11</sup> IR spectra were recorded from Nujol mulls unless otherwise specified. <sup>1</sup>H NMR spectra (250 MHz) were taken with TMS as internal standard. HPLC analyses were performed by using a C-18 SIL-X-10 Perkin-Elmer column. Fluorescence and phosphorescence emissions were determined on a JASCO FP 770 equipped with phosphorimeter in frozen glass (ethanol, pentane, ethyl ether in a 2:5:5 ratio). Flash chromatography was performed by using ethyl acetate or mixtures of light petroleum (fraction boiling in the range of 40–60 °C) and ethyl acetate in varying ratios. Ethanolic (33%) methylamine and dimethylamine, hydrazine monohydrate, *N,N*-dimethylhydrazine, propylamine, and butylamine were obtained from Aldrich Chemical Co. Saturated methanolic ammonia was freshly prepared.

Compounds **1**,<sup>19</sup> **2**,<sup>20</sup> **3**,<sup>20</sup> **13**,<sup>21</sup> **14**,<sup>22</sup> **15**,<sup>21</sup> **27**,<sup>23</sup> **28**,<sup>12a</sup> and **29**<sup>12b</sup> were prepared as reported. All these oxadiazole derivatives except one (**29**) showed similar photophysical behavior with a strong fluorescence emission and weaker phosphorescence. Values of singlet ( $E_s$ ) and triplet ( $E_t$ ) energies (kJ/mol) determined from emission spectra are given in the Table 1. Photochemical reactions were carried out in anhydrous methanol (from Aldrich), by using a Rayonet RPR-100 photoreactor fitted with 16 lamps irradiating at  $\lambda = 254$  nm (in quartz vessels) or at  $\lambda = 313$  nm (in Pyrex vessels) and a merry-go-round apparatus. In the case of analytical photoreactions, quantitative determinations were accomplished by HPLC.

**General Procedure for Photochemical Reactions in the Presence of Nucleophiles.** To a sample of the oxadiazole **1–3** or **13–15** (0.5 g; 2.0–3.0 mmol) in methanol (90 mL) was added a large excess of the appropriate amine [namely: methanolic ammonia (20 mL), ethanolic methylamine or dimethylamine (10 mL), propylamine (5 mL), butylamine (6

mL)] or hydrazine monohydrate (5 mL). The solution was apportioned into two quartz tubes and then irradiated for the time indicated. After removal of the solvent, the residue was suitably worked-up as below. Minor components were discarded.

**Irradiation of Oxadiazoles 1–3 in the Presence of Methylamine.** Irradiation for 1.5 h and chromatography returned starting material (10%) and gave **1-methyl-3-phenyl-1,2,4-triazolin-5-one (6)** (60%), mp 218–219 °C (lit.<sup>24</sup> mp 218–219 °C).

**Irradiation of the Oxadiazole 1 in the Presence of Ammonia, Propylamine, and Butylamine.** Irradiation of **1** (0.5 g) in the presence of methanolic ammonia for 1.5 h, followed by workup of the residue with the minimum of methanol and filtration, gave the **3-phenyl-1,2,4-triazolin-5-one (5)** (0.25 g), mp 325–330 °C (lit.<sup>24</sup> mp 330–332 °C). Chromatography of the mother liquor, besides starting material (0.05 g; 10%) and additional **5** (0.05 g; total yield 60%), gave the ***N*-carbamoylbenzamidine 12** (0.05 g; 10%), mp 132–4 °C (from benzene–ethyl acetate) (lit.<sup>25</sup> mp 135–6 °C), compared with a sample prepared by hydrogenolysis of **1**.<sup>25</sup>

Similarly, irradiation of **1** (0.5 g) in the presence of propylamine for 1.5 h and chromatography gave the **3-phenyl-1-propyl-1,2,4-triazolin-5-one (7)** (0.38 g; 60%), mp 176–178 °C (from aqueous ethanol); IR (KBr pellets) 2680–3150, 1680  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>)  $\delta$  0.88 (t, 3H,  $J = 7.0$  Hz), 1.63–1.78 (m, 2H), 3.67 (t, 2H,  $J = 7.0$  Hz), 7.42–7.81 (m, 5H), 12.19 (s, 1H); MS  $m/z$  203 ( $M^+$ ). Anal. Calcd for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O: C, 65.01; H, 6.45; N, 20.67. Found: C, 65.20; H, 6.60; N, 20.60.

Irradiation of **1** (0.5 g) in the presence of butylamine for 1.5 h gave **1-butyl-3-phenyl-1,2,4-triazolin-5-one (8)** (0.4 g; 60%), mp 146–148 °C (from aqueous ethanol); IR (KBr pellets) 2700–3150, 1685  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>)  $\delta$  0.95 (t, 3H,  $J = 7.0$  Hz), 1.28–1.43 and 1.66–1.77 (2 m, 4H), 3.76 (t, 2H,  $J = 7.0$  Hz), 7.50–8.04 (m, 5H), 12.25 (s, 1H); MS  $m/z$ : 217 ( $M^+$ ). Anal. Calcd for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.50; H, 6.80; N, 19.50.

**Irradiation of the Oxadiazole 1 in the Presence of Dimethylamine.** Irradiation of **1** (0.5 g) for 1.5 h, followed by workup with the minimum of ethyl acetate and filtration, gave  $\alpha$ -**(*N,N*-dimethylhydrazono)-*N*-carbamoylbenzylamine (11)** (0.4 g; 63%), mp 163 °C (from ethyl acetate); IR 3420, 3210, 3140, 1705  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>)  $\delta$  2.52 (s, 6H), 6.49 (s, 2H), 7.35–7.47 (m, 5H), 8.63 (s, 1H); MS  $m/z$  206 ( $M^+$ ). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>N<sub>4</sub>O: C, 58.24; H, 6.84; N, 27.16. Found: C, 58.40; H, 6.70; N, 27.30.

**Irradiation of the Oxadiazole 1 in the Presence of Hydrazine or *N,N*-Dimethylhydrazine.** Irradiation of **1** (0.5 g) in the presence of hydrazine for 1.5 h and chromatography, besides starting material (0.05 g; 10%), gave compound **5** (0.1 g; 20%) and then **1-amino-3-phenyl-1,2,4-triazolin-5-one (9)** (0.2 g; 37%), mp 235–240 °C (lit.<sup>26</sup> mp 235–238 °C). Irradiation of **1** (0.5 g) in the presence of *N,N*-dimethylhydrazine (5 mL) for 1.5 h and chromatography, besides starting material (0.05 g; 10%) and minor components which were discarded, gave **12** (0.3 g; 60%).

**Irradiation of the Oxadiazole 13 in the Presence of Methylamine, Methanolic Ammonia, Dimethylamine, Hydrazine, and *N,N*-dimethylhydrazine.** Irradiation of **13** (0.5 g) in the presence of methylamine for 2 h and chromatography gave starting material (0.3 g; 60%), **1-methyl-3,5-diphenyl-1,2,4-triazole (17)** (0.1 g; 20%), mp 82 °C (from aqueous ethanol) (lit.<sup>27</sup> mp 81.5–82.5), and then traces of **2-phenylquinazolin-4-one (24)** mp 235–237 °C (lit.<sup>1</sup> mp 235–237 °C). Irradiation for 6 h and chromatography, besides starting material (0.05 g; 10%), gave **24** (0.08 g; 16%), **26** (0.06 g; 10%), and **17** (0.15 g; 30%). ***N*-(Methylaminocarbonyl)-*N*-phenylbenzamidine (26)** (or/and its tautomer): mp 160–164 °C (from benzene–light petroleum); IR 3210, 3100, 1680,

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1640  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  2.52 and 2.84 (2d, 3H,  $J = 4.5$  Hz; 2s with  $\text{D}_2\text{O}$ ), 6.68–7.73 (m, 10H), 9.40–9.63 (m, 2H; exchangeable with  $\text{D}_2\text{O}$ ); MS  $m/z$  253 ( $\text{M}^+$ ), 222, 195, 180, 104, 93, 77. Anal. Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$ : C, 71.13; H, 5.97; N, 16.59. Found: C, 71.30; H, 5.80; N, 16.40. Lit.<sup>28</sup> (*Chem. Abstr.*) does not report mp, nor spectroscopic data. Careful hydrolysis of **26** in the presence of hydrochloric acid gave *N*-benzoyl-*N*-methylurea, mp 164–166 °C (from ethanol) (lit.<sup>29</sup> mp 169–170 °C). A sample of **26** has been obtained from ethyl *N*-(methylaminocarbonyl)-*N*-phenylbenzimidate, by adapting the procedure reported.<sup>28</sup>

Similarly, irradiation of **13** (0.5 g) in the presence of methanolic ammonia for 2 h and chromatography, together with starting material (0.3 g; 60%) and traces of **24**, gave **3,5-diphenyl-1,2,4-triazole (20)** (0.05 g; 10%), mp 190 °C (from aqueous ethanol) (lit.<sup>27</sup> mp 191.5–192.5 °C).

Irradiation of **13** (0.5 g) in the presence of dimethylamine for 6 h and chromatography returned starting material (0.08 g; 16%) and gave  $\alpha$ -(*N,N*-dimethylhydrazono)-*N*-benzoylbenzylamine (**23**) (0.3 g; 50%), mp 163 °C (from ethanol); IR 3300, 1670  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  2.72 (s, 6H), 7.34–8.09 (m, 10H), 10.13 (s, 1H); MS  $m/z$  267 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$ : C, 71.89; H, 6.41; N, 15.72. Found: C, 71.80; H, 6.30; N, 15.60. A sample of **23** has been prepared by reacting the methyl *N*-benzoylbenzimidate<sup>24,30</sup> with *N,N*-dimethylhydrazine in methylene chloride.

Irradiation of **13** (0.5 g) in the presence of hydrazine for 6 h and chromatography, besides minor components which were discarded, returned starting material (0.15 g; 30%) and gave **1-amino-3,5-diphenyl-1,2,4-triazole (21)** (0.15 g; 28%), mp 192–195 °C (from ethanol) (lit.<sup>31</sup> mp 195 °C).

Irradiation of **13** (0.5 g) in the presence of *N,N*-dimethylhydrazine (3 mL) for 2 h and chromatography returned starting material (0.3 g; 60%) and gave the *N*-benzoylbenzamidine (0.05 g; 10%), mp 102–103 °C (from hexane) (lit.<sup>32</sup> mp 98–100 °C). Irradiation for 6 h gave starting material (0.1 g; 20%), compound **24** (0.05 g; 10%), and *N*-benzoylbenzamidine (0.2 g; 40%).

**Irradiation of the Oxadiazole 14 in the Presence of Methylamine.** Irradiation of **14** (0.5 g) for 2 h and chromatography returned starting material (0.3 g; 60%) and gave the **2-methoxyquinazolin-4-one (25)** (0.02 g; 4%), mp 230–232 °C (lit.<sup>33</sup> mp 230–232 °C) and then **3-methoxy-1-methyl-5-phenyl-1,2,4-triazole (18)** (0.1 g; 18%), mp 85–86 °C (from light petroleum) (lit.<sup>34</sup> mp 85–86 °C).

**Irradiation of the Oxadiazole 15 in the Presence of Methylamine.** Irradiation of **15** (0.5 g) for 2 h and chromatography returned starting material (0.30 g; 60%) and gave the **1,5-dimethyl-3-phenyl-1,2,4-triazole (19)** (0.1 g; 18%), mp 115–116 °C (from hexane) (lit.<sup>24</sup> mp 115–116 °C). Ir-

radiation for 6 h gave starting material (0.2 g; 40%) and **19** (0.15 g; 28%).

**Irradiation of the 3-(*o*-Aminophenyl)-5-methyl-1,2,4-oxadiazole (27).** A sample of **27** (0.5 g) in methanol (100 mL) was apportioned in eight Pyrex vessels and then irradiated at  $\lambda = 313$  nm for 30 min, when the reaction was complete (by TLC), and the photoproduct **35** partially separated. The solvent was then reduced under vacuum, and the product was filtered to give the **2-(acetylamino)benzimidazole (35)** (0.3 g), mp 315–320 °C (from ethanol) (lit.<sup>35</sup> mp 312–315 °C). Evaporation of the mother liquor and chromatography gave the **3-(acetylamino)indazole (32)** (0.1 g; 20%) mp 200–204 °C (from water) (lit.<sup>12a</sup> mp 204 °C), and then additional **35** (0.05 g; total yield 70%). Analytical photochemistry [compound **27** (20 mg) in methanol (10 mL) was irradiated for 20 min, when conversion of starting material was complete] gave **32** (25%) and **35** (75%). Parallel irradiations (at  $\lambda = 313$  nm) in the presence of piperylene or in the presence of methylamine, or irradiations (at 360 nm) in the presence of benzophenone, did not show any significant change.

**Irradiation of 3-[*o*-(Methylamino)phenyl]-5-methyl-1,2,4-oxadiazole (28).** Irradiation (at  $\lambda = 313$  nm, 30 min) of **28** (0.5 g) in methanol (100 mL) apportioned in eight pyrex vessels and chromatography gave the **3-(acetylamino)-1-methylindazole (33)**, (0.15 g; 30%), mp 142 °C (from water) (lit.<sup>12a</sup> mp 142 °C), and then the **2-(acetylamino)-1-methylbenzimidazole (36)** (0.25 g; 50%), mp 182 °C (from methanol) (lit.<sup>36</sup> mp 182 °C). Analytical photochemistry as above gave **33** (30%) and **36** (70%).

**Irradiation of 3-(*o*-Aminophenyl)-5-phenyl-1,2,4-oxadiazole (29).** After irradiation (at  $\lambda = 254$  nm, 3 h) of compound **29** (0.25 g) in methanol (100 mL) apportioned in eight quartz vessels (when the conversion of starting material was complete), the solvent was removed and the residue was taken up with the minimum of ethanol and filtered to give the **2-(benzoylamino)benzimidazole (37)**, (0.2 g), mp 235–237 °C (lit.<sup>37</sup> mp 235–240 °C). Evaporation of the mother liquor and chromatography gave additional **37** (0.05 g; total yield 50%) and then the **3-(benzoylamino)indazole (34)** (0.2 g; 40%), mp 162–165 °C (from benzene) (lit.<sup>12b</sup> mp 161 °C). Analytical irradiations gave **34** (45%) and **37** (55%). Analytical irradiations of **29** at  $\lambda = 313$  nm in Pyrex vessels (4 h) gave the following composition of the photolysate: starting material **29** (50%), **34** (15%), **37** (35%). Irradiations of **29** in the presence of piperylene (at  $\lambda = 254$  nm) or benzophenone (at  $\lambda = 360$  nm) gave no changes.

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