# Photoinduced β-Elimination of the Triazole Group in the 1-(N,N-Bisacyl)amino-1,2,3-triazoles

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# Dedicated to the memory of Dr. Roland K. Robins

The photoelimination of the 1,2,3-triazole group from the title compounds proceeds, depending upon the reaction conditions, via an intra- or intermolecular hydrogen abstraction or electron-transfer mechanism, followed by homolytic cleavage of the N,N bond. It can also proceed via  $\pi^*$ -assisted  $\beta$ -cleavage of the same weak bond, when light of shorter wavelength is used. The composition of the products suggests that in all cases most probably a  $\sigma$ -type 1,2,3-triazolyl radical 10 is eliminated which is further quenched by hydrogen or chlorine abstraction.

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Imides give most of the major photochemical reactions known for the simple carbonyl system and several unprecedented reactions as well [1]. As a general rule, when N-substituted phthalimides and other cyclic imides undergo hydrogen abstraction from the  $\gamma$  (or, less frequently) from the  $\delta$  position of the N-substituent, they yield mainly the cyclization products of the resulting 1,4- or 1,5-diradical. On the other hand, the products of type II elimination are isolated only in small amounts. On one occasion the dominant reaction was type II cleavage which resulted the elimination of an N-ethyl substituent presumably as ethylene [2]. For both aromatic and aliphatic acyclic imides, however, the primary photochemical reaction is mainly the fission of a N-CO bond and no type II process is observed involving the N-substituent even when the abstractable hydrogen is tertiary [3].

In this report we wish to exploit the presence of a weak N-N bond in the  $\beta$ -position of an imidic chromophore, a situation pertaining to the title 1-(N,N-bisacyl)amino-1,2,3-triazoles **2**, in order to demonstrate that the known pattern of photochemical reactivity, as exemplified above for this chromophore, is completely altered. In particular we are interested in presenting the first example of a  $\beta$ -cleavage reaction of an imidic carbonyl, which proceeds, depending

upon the reaction conditions, via an intra- or intermolecular hydrogen abstraction,  $\pi^*$ -assisted cleavage, or electron transfer mechanism. It is of interest to note that there are only a few examples of  $\beta$ -cleavage reactions involving carbonyl compounds outside those reported for ketones containing good radical leaving groups on the  $\alpha$ -carbon [4] and that, to our knowledge, in none of these reactions the cleavage of a semipinacol to a neutral molecule and a free radical is implicated (vide infra).

Finally, we also wish to contribute a rare example of an unsensitized photochemical reaction involving a 1*H*-1,2,3-triazole derivative in which the triazole group remains intact [5] and does not extrude nitrogen upon irradiation [6] and, the isolation therefrom of products supporting the intermediacy of the hitherto unknown 1,2,3-triazolyl radical 10.

# Results and Discussion.

Several years ago when we were affecting the photochemical isomerization of 4,5-dimethyl-1-[( $\alpha$ -benzoyloxy)-benzylideneamino]-1,2,3-triazole (isoimide **1a**) to 4,5-dimethyl-1-(N,N-dibenzoyl)amino-1,2,3-triazole (imide **2a**) we noticed that, upon prolonged irradiation, product **2a** decomposed yielding dibenzamide [7] (**4a**, Scheme 1). Since

the photolysis of 2a to 4a represented a formal  $\beta$ -cleavage reaction, examples of which, as already has been mentioned, are scarcely available in the literature of organic photochemistry [4,8] and since this photoreaction did not conform to the established patterns of photochemical reactivity for the N-substituted imide system [1] we decided to undertake this study.

The open chain imides **2a-g** and the phthalimides **23** were photolyzed in two different ways. In the first, light from a medium pressure mercury arc filtered through Pyrex was used ( $\lambda > 280$  nm), while in the second irradiation from the same light source was passed through quartz and therefore included also the short wavelength region of its spectrum ( $\lambda > 220$  nm). These two different irradiation conditions represent a crude yet valid approach to examine any wavelength-dependence of the reaction under study.

We found that, upon irradiation in various solvents through Pyrex, the 1,2,3-triazolimides 2, with the noted exception of 2c and 2g, which were unreactive, all yielded fair-to-good amounts of the corresponding imides 4 (Scheme 1). Of the reactive triazolimides 2 all except the 4,5-dimethyl substituted such 2a and 2b, gave also the corresponding 1(2)H-1,2,3-triazoles 3. From the reaction mixture were occasionally isolated substituted benzamides 5 and benzoic acids 6 which, as control experiments indicated, resulted from the decomposition of 4 on the silica gel column used for product isolation.

It can be seen from the results summarized in Table 1, that the photoreactivity of **2a** and **2e**, as indicated by their respective irradiation times, parallel the hydrogen-donating ability of the solvents [9] (entries 1-5 and 14-15). Furthermore, the 4,5-dimethyl-1,2,3-triazole derivative **2a** reacts much faster than the corresponding 4,5-diphenyl derivative **2e** (entry 2 vs 14).

Photosensitization of the reaction with benzophenone was successful and resulted in the same product ratio with that of the unsensitized reaction with much shorter irradiation times. It was asserted that the energy transfer from the benzophenone triplet to the triplet of **2a** was exothermic by the quenching of benzpinacol formation in an irradiated, in the presence of imide **2a**, solution of benzophenone in isopropyl alcohol. The photoreaction of **2a** was completely quenched by naphthalene [10].

Both the triplet photosensitization and the naphthalene quenching strongly argue in favor of the triplet as the responsible excited state for the reaction. As far as the configuration of this state is concerned we propose, on the basis of the exhibited H-abstracting ability [11], an  $n, \pi^*$  state. Naturally, N,N-bis-naphthoylamino-1,2,3-triazoles 2c and 2g, which are expected by analogy with acetonaphthone and naphthophenone to have a low lying  $\pi, \pi^*$  triplet, must owe their photostability to the inability of this state to abstract hydrogen efficiently [12]. However, it is still possible that the reactive imides have low lying  $\pi, \pi^*$  triplet states, but reactivity takes place predominantly

Table 1
Products from the Irradiation [a,b] of 1,2,3-Triazolimides 2 in Various Solvents

Entry	Substrate	Solvent	Irradia time/h	ation ours [c]	3	Produ 4	cts, Isola 5	ted yields/	% <b>7</b>	8
	_									
1	2a	MeCN	20	[a]		49	8	13		
2	2a	PhH	12	[a]		<b>52</b>	15	10		
2 3	2a	MeOH	9	[a]		60	10	13		
4	2a	i PrOH	3	[a]		60	8	11		
4 5	2a	PhSH	2.5	[a]		60	8	12		
6	2a	PhH	4	[b]		64			8	
6 7	2a	MeOH	4	[b]		62				
8	2a	i PrOH	3	[b]		59				
9	2ь	PhH	3	[b]		61				
10	2c	PhH	110	[a,d]						
11	<b>2</b> e	i-PrOH	50	[a,d]						
12	<b>2</b> e	PhH	2.5	[b]		59			6	
13	2d	PhH	2.5	[b]	52	49				
14	<b>2e</b>	PhH	80	[a]	41	32	6	8		
15	<b>2e</b>	i- PrOH	12	[a]	47	39	11	9		
16	<b>2e</b>	MeCN	4	[b]	57	59				
17	<b>2e</b>	PhH	4	[b]	59	59		9		
18	<b>2e</b>	MeOH	4	[b]	59	61				
19	<b>2e</b>	i PrOH	3	įβį	60	61				
20	<b>2e</b>	PhSH	6	[b]	64	60				
21	<b>2e</b>	PhCl	4	[b]	48	46				5
22	21	PhH	3	[ь]	54	59				
23	2g	• PrOH	50	[a,d]						
24	2g	PhH	2.5	[b]	61	60			9	

<sup>[</sup>a] 400 Watt medium-pressure mercury arc through Pyrex filter. Solutions were deaerated with nitrogen prior their irradiation. [b] Same as above but through quartz. [c] For >90% reaction. Substrate concentration 25 mM. Scale for **2e** and **2g** one-tenth the usual. [d] With 100% recovery of starting material.

from the thermally populated  $n, \pi^*$  state which lies nearby, as it has been suggested for phthalimides [13].

We propose the following tentative mechanism for the photolysis of 2 with Pyrex filtered light (Scheme 2, path a). Excited imides 2 in their  $n, \pi^*$  triplet state abstract hydrogen from the solvent to give the semipinacol radical 9, or alternatively, when possible (R2 = Me) intramolecularly (δ-H-abstraction). In the latter case the 1,5-diradical 13 results. Formation of 9 or 13 is followed by N-N bond cleavage and it is induced by the attainable favorable overlap of this weak bond (dissociation energy [14] 159.2 kJ·mol<sup>-1</sup>) with the p orbital bearing the odd electron. Ketyl radical 9 cleaves to the 1,2,3-triazolyl radical 10 which after hydrogen abstraction gives 1(2)H-1.2.3-triazole 3 and the enol form of benzamide 11. On the other hand, biradical 13 yields 11 and other unidentified products. It follows that, while 5-methyl substituted imides such as 2a and 2d are expected to react primarily by the relatively favourable &hydrogen abstraction [15], they are also capable of reacting in an intermolecular way (Scheme 2, path a).

When the irradiation of the imides 2 was carried through quartz, two important differences emerged. First, the reactivity did not vary with the medium (entries 6-7 and 16-21), implying a rate determining step in which the solvent does not participate and second, the inactive, under the previous conditions (Pyrex), bis-naphthoylimides 2c and 2g were as reactive as the other imides. Also, the reaction which could not be quenched by naphthalene, nor sensitized (for 2g) with benzophenone, showed a remarkable temperature dependence (Table 2).

Table 2
Temperature Dependence of the Photolysis of 1-(N,N-Bisacyl)amino-1,2,3-triazoles **2e** and **2g** in Benzene

Entry	Imide	Filter	Irr. time [a]/min. Temperature		
			20°	80°	
1	2e[b]	Pyrex	>900	300	
2	<b>2e</b> [b]	Quartz	40	15	
3	<b>2g</b> [c]	Pyrex	>900	420	
4	2g [c]	Quartz	5 5	20	

[a] Full consumption of the starting material. [b] Concentration 25 mM. [c] Concentration 10 mM.

We believe that in this case, where light of shorter wavelengths can be absorbed, the primary photochemical process is a  $\pi^*$ -assisted  $\beta$ -cleavage reaction leading to the 1,2,3-triazolyl and imidyl radicals 10 and 12 (Scheme 2, path b). Both radicals 10 and 12 are quenched by hydrogen abstraction to yield products 3 and 4.

The relatively high yields of 1(2)H-1,2,3-triazoles **3** and dibenzamides **4** and the observation of radical coupling products from the solvent (biphenyl (7) and 4,4'-bischlorobiphenyl (8)) indicate that either the 1,2,3-triazolyl radical **10** or the imidyl radical **12** or, most likely, both can abstract hydrogen. This disputes a possible heterolytic fragmentation of the N-N bond.

Ultraviolet and fluorescence spectra of the various imides 2 were measured in benzene and acetonitrile (Table 3). That the lowest energy transition is  $\pi, \pi^*$  is evident from the bathochromic shift in acetonitrile and the rather large extinction coefficients [16].

Table 3

Absorption and Fluorescence Maxima of 1-(N,N-Bisacyl)amino1,2,3-triazoles 2 in Benzene and Acetonitrile

Imide	Absor λ max (lo		Emissi λ max/		
	PhH	MeCN	PhH	MeCN	
2a	300 (3.05)	307 (3.07)	364	392	
2c	307 (3.98)	313 (3.38)	442	457	
2 d	300 (3.21)	308 (3.20)	364	366	
<b>2e</b>	301 (3.30)	$312 \ (3.21)$	366	400	
2g	305 (4.25)	308 (3.90)	442	457	
23a	304 (3.22)	306 (3.12)	380	382	
23ь	303 (3.04)	304 (3.44)	372	380	

For the naphthoyl imides 2c and 2g, which are inert, when irradiated with long-wavelength light, implication of a vibrationally excited singlet seems very probable [17]. The temperature dependence of the reaction (Table 2) also supports this conclusion. In the case of the other imides 2, however, a very reactive and, therefore unquenchable,  $n, \pi^*$  or  $\pi, \pi^*$  triplet state could have a moderate contribution to the  $\beta$ -cleavage reaction as well.

It is proposed that the reactive state is stabilized by coupling of the carbonyl  $\pi^*$  with the N-N  $\sigma^*$  orbital. This coupling, which weakens the N-N bond, would require it to be perpendicular to the carbonyl [18] (structure 14). In fact, the results of X-ray analysis [19] and evidence gathered from the study of the dipole moments [20], indicate that, both in the solid state and in solution the 1-(N,N-bisacyl)-amino-1,2,3-triazoles 2 exist preferentially in such conformations. Furthermore, the fact that the 1-(N-phthalimido)-1,2,3-triazoles 23, which are unable for steric reasons to attain such conformations, were very sluggish in their reaction (vide infra), gives additional support to the above proposition.

In our efforts to find conditions equally effective for the photoelimination of the triazole group from 1,2,3-triazolimides 2 with both  $n, \pi^*$  or  $\pi, \pi^*$  lowest triplet states, we have also irradiated the title imides in acetonitrile solution and in the presence of triethylamine (15) (electron-transfer conditions). We found that, in all cases studied (Table 4), very good yields of dibenzamides 4 were obtained. Imides 2d-g gave also very good yields of the corresponding 1(2)H-1,2,3-triazoles 3. The proposed electron-transfer mechanism is outlined in Scheme 3.

1) 2 hv 2S<sub>1</sub> isc 2T<sub>1</sub>
2) 
$$(C_2H_5)_3N + 2(S_1 \text{ or } T_1)$$
  $(C_2H_5)_3N^{++} + \begin{pmatrix} R^1 & R^2 & O \\ & & & \\ &$ 

Step 1 is excitation of the imide 2 to its singlet or (via intersystem crossing) to its triplet state. The ultraviolet absorption spectra of mixtures of the imides 2 and triethylamine in acetonitrile were the composite of the individual spectra; there was no evidence of complex formation be-

tween the ground-state molecules.

In step 2 electron-transfer from the ground-state triethylamine (donor, D) to the excited state 2 (acceptor, A) takes place, ultimately leading to the free radical ions 16 and 17. Although we did not detect any exciplex emission, the implication of such an intermediate, during step 2, remains a possibility, since exciplex emission is not the rule [21] especially in polar solvents.

Proton transfer from 16 to 17, during step 3, yields the semipinacol radical 9 and radical 18. The former is further transformed, as exemplified already in Scheme 2, to products 3 and 4.

Alternatively, cleavage of the anion radical 17 leading to the radical 10 and to the anion 19 could be envisioned. The choice between these two possibilities is difficult, since it requires knowledge of the rates for the N-N fragmentation and proton transfer steps.

That the singlet state of 2 is reactive follows from the observed fluorescence quenching of 2c by 15. This type of quenching is energetically feasible. The free-energy changes ( $\Delta G$ ) for this process, estimated using the well known Weller equation [22], together with the electrochemically determined half-wave potentials and, the singlet energies of the compounds involved, are given in Table 5.

Table 4

Products from the Irradiation [a] of 1,2,3-Triazolimides 2 in Acetonitrile Solution in the Presence of Triethylamine

Entry	Substrate	Irradiation time/hours [b]	Products Isolated Yields/ <sup>4</sup> <b>3</b> 4		
1	<b>2a</b> [c]	6		72	
2	<b>2</b> e [d]	3		68	
3	<b>2d</b> [e]	4	70	71	
4	<b>2e</b> [c]	7	72	75	
5	<b>2g</b> [d]	3	71	$\boldsymbol{\Theta}$	

[a] 400 Watt medium-pressure mercury arc through Pyrex filter. Solutions were deaerated with nitrogen prior their irradiation. [b] For >90% reaction. Substrate concentration: [c] 25 mM, [d] 12.5 mM, [e] 16.5 mM.

It can be seen that, in all cases the electron-transfer is exergonic for the singlet ( $\Delta G < 0$ ). The same can be said about the triplet, if it is assumed, on the basis of the triplet quenching experiments, that the triplet energies of the imides 2 are higher than the triplet energy of naphthalene [23] ( $E_T = 255.2 \text{ kJ} \cdot \text{mol}^{-1}$ ).

In every photoreaction described above, we have implied the intermediacy of the triazolyl radicals 10 to account for the formation of 1(2)H-1,2,3-triazoles 3. In order to support our hypothesis and, to further probe the reactivity of this interesting heterocyclic free radical, we have irradiated, under the most effective conditions for  $\beta$ -cleavage (quartz filter), the imides 2a, 2d and 2e in carbon

Table 5

Redox Potentials, Singlet Energies and Calculated △C Values for Electron-Transfer from Triethylamine (15) and N,N-Dimethylaniline (20) (Donors, D) to Imides 2 (Acceptors, A) in Acetonitrile

Entry	Substrate	abstrate ${ m E}_{1/2}^{ m Red}\left( { m A} ight)\left[ { m a,b} ight]$ /V		ΔΕ <sub>0,0</sub> (A) [e] /kJ.mol <sup>-1</sup>	∆G [f] /kJ.mol <sup>-1</sup>	
					15	20
1	2a	-1.67 [c]		360.8	-123.6	-137.0
2	<b>2</b> c	-1.44 [c]		329.8	-93.9	-107.3
3	2d	-1.57 [c]		356.6	-129.1	-142.5
4	<b>2e</b>	-1.62 [c]		338.6	-106.0	-119.4
5	<b>2</b> g	-1.41 [c]		332.7	-120.7	-134.1
6	23a	-1.25 [dj		358.2	-161.9	-175.4
7	23b	-1.18 [dj		339.8	-150.2	-163.7
8	15		+0.84 [c]			
9	20		+0.70 [c]			

[a] Obtained by cyclic voltametry: Pt electrode, tetraethylammonium perchlorate (0.1 M) in acetonitrile solution, vs SCE. [b] Taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential (R. S. Nicholson, Anal. Chem., 38, 1406 (1966)). [c] The process was not reversible, the half-wave potential was estimated using the 50 mV/s sweep rate. [d] The process was quasi-reversible, the half way potential was estimated using the 50 mV/s sweep rate. [e] The point of intersection of the absorption and emission spectra was taken as the singlet energy. [f] Calculated with the aid of the equation:  $\Delta G = 96.55[E_{1/2}^{Ox}(D)_V - E_{1/2}^{Red}(A)_V - e_0^2/\epsilon\alpha] - \Delta E_{0.0}$  kJ.mol<sup>-1</sup>; assuming  $\alpha = 7$  Å (D. Rehm and A. Weller, Isr. J. Chem., 8, 259, (1970)) and  $\epsilon_{25} = 36.7$  [22].

Table 6

Products from the Irradiation [a] of 1,2,3-Triazolimides 2 in

Carbon Tetrachloride

Entry	Substrate	Irradiation time/hours	Products Isolated Yields/%			
		[b]	21	3	4a	
1	2a	4	22		78	
2	2d	4	53	20	79	
3	<b>2e</b>	2.5	53	20	81	

[a] 125 Watt medium-pressure mercury arc (quartz cooling jacket) immersed in the irradiated solution. [b] For >90% reaction. Substrate concentration 12.5 mM.

tetrachloride (Scheme 4). In all cases fair-to-good yields of 1-chloro-1,2,3-triazoles 21 and very good yields of dibenzamide 4a were obtained (Table 6). We also isolated 1(2)H-1,2,3-triazoles 3d and 3e in small yields, from the hydrolysis of the corresponding 1-chlorotriazoles 21, which occurred during workup [24].

From the above results it is apparent that, the 1,2,3-triazolyl radical 10 is not capable of forming C-chlorinated products. The same can be claimed about the formation of C-N- or C-C-dimerization products [25,26] and these facts imply a  $\sigma$ -type radical.

The above conclusion, however, seems incompatible

Scheme 4

R<sup>1</sup>

$$R^2$$
 $R^2$ 
 $R^1$ 
 $R^2$ 
 $R^2$ 
 $R^1$ 
 $R^2$ 
 $R$ 

with the preliminary results of calculations performed for radical 10, which have indicated that its ground-state is a  $\pi$ -type doublet [27]. Similar situation pertains to the 1-pyrazolyl radical, for which calculations predict a ground-state  $\pi$ -type radical [28], while reactivity backs a  $\sigma$  type [29]. A viable explanation is that the triazolyl radical 10, like the pyrazolyl one, can live long enough to react as a metastable  $\sigma$ -type radical before decaying to its  $\pi$ -type ground-state.

Finally, for the purpose of extending the scope of the present work to the most extensively studied class of imides, the phthalimides, we have examined the photolysis of 1-(N-phthalimido)-4,5-dimethyl-1,2,3-triazole (23a) and of 1-(N-phthalimido)-4,5-diphenyl-1,2,3-triazole (23b).

It was found that both phthalimides 23a and 23b remained practically unchanged, when irradiated through Pyrex in benzene or isopropyl alcohol for prolonged periods of time.

We attribute this photostability to either, a  $\pi \to \pi^*$  configuration of the lowest energy excited state and its concomitant inefficiency towards *H*-abstraction, or to the inability of the semipinacol radical **24** (Scheme 5) to cleave for stereoelectronic reasons. The first assumption is supported, for the singlet, by the observed bathochromic shift of the absorption maxima on going to more polar solvents

(Table 3) [16]. With respect to the second assumption, model inspection reveals that the rigidity of the five-membered planar phthalimido group does not permit interaction of the N-N bond with the p orbital bearing the lone electron. The same holds true for the interaction of this N-N bond with the  $\pi^*$  orbital of the excited carbonyl and explains the inefficient primary phorochemical  $\beta$ -cleavage reaction of phthalimides 23, which will be discussed afterwards.

Analogous reactivity, or lack therefrom was reported for hydrazides 25 [30] and 26 [31] respectively and, in our opinion, this observation also manifests the same stereo-electronic effect.

When 1-(N-phthalimido)-1,2,3-triazoles 23 were irradiated through quartz and for irradiation times at least twentyfold those required for the open-chain imides 2,  $\beta$ -cleavage to the triazolyl radical 10 and to the phthalimidyl radical 27 took place (Scheme 5). This finding differs from earlier reports suggesting that 23b was photostable [32].

Table 7
Products from Irradiation [a] of 1-(N-Phthalimido)-1,2,3-triazoles 23 in Various Solvents

Entry	Substrate	Solvent	Irradiation time/hours	Products Isolated Yields/%			
			[b]	3	21	28	29
1	23a	PhH	215			42	
2	23a	<i>i</i> -PrOH	135				
3	23b	PhH	120	56		60	67
4	23ь	<i>i</i> -PrOH	123	58			61
5	23Ь	CCl <sub>4</sub>	115	44	21		60

[a] 400 Watt medium-pressure mercury arc through quartz. [b] For >90% reaction.

In Table 7 the final products, which result from the reaction of radicals 10 and 27 with the solvent, are given.

The isolation in good yields of N-phenylphthalimide (28) and phthalimide (29) indicates the formation of the phthalimidyl radical 27 which, as expected for imidyl radicals, attacks benzene [33] or abstracts hydrogen [34]. It also underscores the significance of the reaction as a potential method for the synthesis of the industrially important N-arylphthalimides [35]. On the other hand, triazolyl radical 10 gave the expected products 3 and 21 in good yields presumably via routes described earlier (Schemes 2 and 4).

In conclusion, the photolysis of the title compounds can serve as a convenient method for the generation of the 1,2,3-triazolyl radical 10 and the imidyl radicals 12 or 27, under mild conditions. Some of the products derived from these radicals, such as the chlorotriazoles 21, or the N-phenylphthalimide 28 are important reagents with synthetic and/or industrial value and are generated under the most favorable conditions (i.e. avoidance of oxidative environment [24] for 21, anhydrous conditions [36] for 28). Furthermore, 2a was found to be a very efficient photoinitiator for the photopolymerization of methyl methacrylate [37].

Finally, since the present photoreaction is due to the existence of the weak N-N bond in the  $\beta$ -position of the imidic chromophore, it can potentially be extended to a variety of N-heterocyclic imides for the purpose of generating other nitrogen containing heterocyclic radicals, for which efficient methods of formation are in need.

#### EXPERIMENTAL

# Materials.

All solvents used were purchased from Fluka and purified according to established procedures [38]. Flash column chromatographies were performed using Merck silica gel 60 (230-400 mesh) and mixtures of petroleum ether (bp 40-60°) - ethyl acetate of increasing polarity as eluant. Isoimides 1a [39], 1b [40], 1c [41], 1d [42], 1e [43], 1f [44] and 1g [41] were prepared as described in the literature and subsequently isomerized thermally or photochemically to the corresponding imides 2. The isomerization gave the products 2a [45], 2b [40], 2c [41], 2d [40], 2e [45], 2f [19] and 2g [41] which were identified from their reported mp's and spectra.

Compounds 23a and 23b were prepared from the corresponding 1-amino-1,2,3-triazoles and phthalic anhydride [32]. Authentic samples, used for the identification (undepressed mixed mp and identical ir spectra) of each one of the photoproducts, were either commercially purchased or, as in the case of 3e [46], 3d [47], 4a [48], 21 [24] and 28 [49], prepared according to reported procedures. Photochemical reactions were carried out using commercially available 125 or 400W medium pressure mercury lamps at 20°, unless otherwise stated.

# Physical Data.

The uv spectra were recorded with a Shimadzu UV-210A spectrophotometer while fluorescence spectra with a Fluorispec SF1 spectrofluorometer; the latter are uncorrected. Cyclic voltametric data were obtained using a three-electrode cell with a Wenking LB 75M potentiostat connected with Wenking VSG 72 trigonal pulse generators. The reference electrode was saturated calomel (SCE) and the supporting electrolyte 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile. The substrate concentrations were typically 0.001 M. The reactions were monitored by tlc using pre-coated 0.25 mm Merck silica gel 60 F<sub>254</sub> plates.

Irradiation of 4,5-Diphenyl-1-(N,N-dibenzoyl)amino-1,2,3-triazole (2e) in Benzene Solution.

A solution of **2e** (444 mg, 1 mmole) in 40 ml of benzene was irradiated in a Pyrex vessel, using a 400W medium pressure mercury arc at 20°, until **2e** was largely consumed (80 hours). Evaporation of the solvent, and chromatography of the residue on a silica gel flash column, using a mixture of petroleum ether-ethyl acetate as eluant, gave the following products: dibenzamide (**4a**, 72 mg, 32%), 1(2)H-4,5-diphenyl-1,2,3-triazole (**3e**, 91 mg, 41%), benzoic acid (**6a**, 10 mg, 8%) and, benzamide (**5a**, 7 mg, 6%).

According to the general procedure described above all direct irradiations of imides 2 in various solvents were carried out. Irradiation conditions and isolated product yields are summarized in Table 1.

Irradiation of **2e** in the Presence of Triethylamine in Acetonitrile Solution (Electron-Transfer Reaction).

A solution of **2e** (222 mg, 0.5 mmole) and 1 ml of triethylamine in 20 ml of acetonitrile was irradiated in a Pyrex vessel at 20°, until **2e** was largely consumed (7 hours). Evaporation of the solvent, and chromatography of the residue on a silica gel flash column using a mixture of petroleum ether-ethyl acetate as eluant, gave the following products: **4a** (84 mg, 75%) and **3e** (79 mg, 72%).

All irradiations under electron-transfer conditions were done as described above and the results are depicted in Table 4. Irradiation of 2e in Carbon Tetrachloride.

A solution of 2e (444 mg, 1 mmole) in 100 ml of dry carbon tetrachloride was irradiated through Quartz at 5° until the starting material was practically consumed (4 hours). After solvent evaporation and flash column chromatography on silica gel using a mixture of petroleum ether-ethyl acetate as eluant, the following products were obtained: 1-chloro-4,5-diphenyl-1,2,3-triazole (21e, 155 mg, 53%), 4a (175 mg, 78%) and 3e (44 mg, 20%).

Irradiation of **2a** and **2d** under the above conditions gave, after workup, the 1-chloro-1,2,3-triazoles **21a** and **21d** respectively (Table 6). Both products were isolated as unstable oils and identified from their mass spectra [24]. Product **21d** was also hydrolyzed to **3d** in a further attempt to prove its structure.

Irradiation of 1-(N-Phthalimido)-4,5-diphenyl-1,2,3-triazole (23b) in Benzene Solution.

A solution of **23b** (183 mg, 0.5 mmole) in 100 ml of dry benzene was irradiated through Quartz until **23b** was largely consumed (120 hours). After solvent evaporation and preliminary column chromatography on silica gel, in order to remove the polymeric material, the mixture was rechromatographed on a silica gel flash column, as described above, and gave the following products: *N*-phenylphthalimide (**28**, 67 mg, 60%) and **3e** (62 mg, 56%).

The irradiations of the other 1-(N-phthalimido)-1,2,3-triazoles 23 in various solvents, which were carried out in accordance with the above procedure, are summarized in Table 7.

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