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Mechanistic Investigations into the Photochemistry of 4-Allyl-tetrazolones in Solution: A New Approach to the Synthesis of 3,4-Dihydro-pyrimidinones

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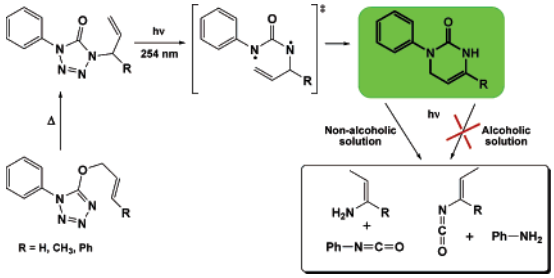

Photolysis ($\lambda = 254$ nm) of 4-allyl-tetrazolones **2a**−**c** was carried out in methanol, 1-propanol, 1-hexanol, acetonitrile, and cyclohexane. The sole primary photochemical process identified was molecular nitrogen elimination, with formation of pyrimidinones **6a**−**c**. Following the primary photocleavage, secondary reactions were observed in acetonitrile and cyclohexane, leading to phenyl-isocyanate (**7**), aniline (**9**), and 1-phenylprop-1-enyl-isocyanate (**10a**). In alcoholic solutions, the primary products, **6a**−**c**, remained photostable even under extended irradiation, making possible the isolation of 3,4-dihydro-pyrimidinones as stable compounds in very high yields. The observed photostability of pyrimidinones **6a**−**c** in alcohols is ascribed to the excited state quenching via reversible proton transfer, facilitated by the solvent cage stabilization due to formation of hydrogen bonds. The viscosity of alcohols is directly related to the cage effects observed. The photocleavage of 4-allyl-tetrazolones leads probably to a caged triplet radical pair. This hypothesis is confirmed by the solvent viscosity effect on the photolysis quantum yields. Additionally, dissolved molecular oxygen sensitizes the formation of pyrimidinones, as should be expected for a triplet intermediate that can only form the product molecule after T−S conversion, which is accelerated by oxygen.

Introduction

Tetrazole (CN_4H_2)[1] and its derivatives have drawn widespread attention as a result of their practical applications. The tetrazolic acid fragment, $-CN_4H$, has similar acidity to the carboxylic acid group, $-CO_2H$, and is almost isosteric with it but is more stable metabolically.[2] Hence, replacement of $-CO_2H$ by $-CN_4H$ groups in biologically active molecules has been widely applied in research areas of major interest.[3] The tetrazolic ring is also featured in the structure of many highly efficient drugs.[4−6] A wide range of tetrazole derivatives has been patented for

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(1) Bugalho, S. C. S.; Maçôas, E. M. S.; Cristiano, M. L. S.; Fausto, R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3541.
(2) (a) Singh, H.; Chawla, A. S.; Kapoor, V. K.; Paul, D.; Malhotra, R. K. *Prog. Med. Chem.* **1980**, *17*, 151. (b) Kimura, T.; Shuto, D.; Hamada, Y.; Igawa, N.; Kasai, S.; Liu, P.; Hidaka, K.; Hamada, T.; Hayasshi, Y.; Kiso, Y. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 211.
(3) Noda, K.; Saad, Y.; Kinoshita, A.; Boyle, T. P.; Graham, R. M.; Husain, A.; Karnik, S. S. *J. Biol. Chem.* **1995**, *270*, 2284.
(4) Mavromoustakos, T.; Kolocouris, A.; Zervou, M.; Roumelioti, P.; Matsoukas, J.; Weisemann, R. *J. Med. Chem.* **1999**, *42*, 1714.
(5) Toney, J. H.; Fitzgerald, P. M. D.; Grover sharma, N.; Olson, S. H.; May, W. J.; Sundelof, J. G.; Vanderwall, D. E.; Cleary, K. A.; Grant, S. K.; Wu, J. K.; Kozarich, J. W.; Pompliano, D. L.; Hammond, G. G. *Chem. Biol.* **1998**, *5*, 185.

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antihypertension activity and as angiotensin II receptor antagonists, useful for treating congestive heart failure and in preventing cardiac hypertrophy. The tetrazolic ring has also been used to modify the structure of the heme environment in myoglobin through incorporation of the *N*-tetrazol-5-yl histidine unit.[7] The 3′-tetrazolo-3′-deoxythymidines were the first approved drugs for AIDS treatment, and several tetrazole derivatives have been explored for antituberculotic activity.[8,9] Furthermore, a wide range of compounds with the tetrazol-1-yl acetic acid structure have been claimed as aldose reductase inhibitors for the treatment and prevention of diabetes complications. Tetrazoles are also used as artificial sweeteners, plant growth regulators, herbicides and fungicides,[10] in photography,[11] and as gas-generating agents in airbags.[12]

The relevance of tetrazolyl compounds stimulated research in their structure and reactivity. Special attention has been devoted to heteroaromatic ethers derived from tetrazole, with important practical uses as intermediate compounds in the transformation of alcohols.[13−15] Compounds bearing an allylic alcohol function are often vital structural units of biologically active systems and have also attracted widespread attention as key intermediates in synthesis.[16] Previously, we have reported that selective hydrogenolysis of the C−OH bond of allyl alcohols can be achieved conveniently by first reacting the alcohol with a 5-chloro-1-aryltetrazole[17] so as to form the heteroaromatic allyl ether **1**, Figure 1, which will then undergo smooth heterogeneously catalyzed transfer hydrogenolysis to form the alkene **3**, corresponding to the allyl group, and the aryltetrazolone **4**.[18] In ethers **1**, which can be regarded as imidates, the heteroaromatic group together with an oxygen atom from the original allyl alcohol acts as an excellent leaving group in catalyzed ipso substitutions.

A selective heterogeneous catalytic transfer reduction of such allyl ethers is quite remarkable, because it successfully competes with hydrogenation of the double bond and also with the relatively easy [3,3]-sigmatropic rearrangement to give the

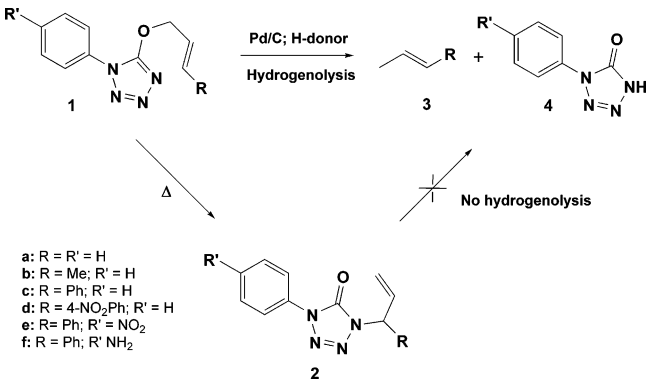


FIGURE 1. Hydrogenolysis and thermal isomerization of 5-allyloxy-1-aryl-tetrazoles.

N-allyl isomers **2**.[19] Thermal *O* to *N* migration of the allyl group in a series of 5-allyltetrazolyl compounds **1**, Figure 1, proceeds exclusively in a [3,3] sense through a polar chairlike transition state, to give *N*-allyl-tetrazolones **2** as sole products.[19] This behavior is similar to the notionally comparable general Cope rearrangement, which proceeds through an allowed [3,3] mechanism.[20]

Tetrazoles are known to exhibit a very interesting and rich photochemistry. A literature survey revealed that photolysis of 1,4-dihydro-5*H*-tetrazole derivatives, both in solution and isolated in low-temperature matrixes, generally results in the elimination of N_2. However, in several cases, it is unknown whether the loss of N_2 and formation of the final products occurs in a concerted process or whether biradicals or zwitterions are involved as intermediates.[21] In other substituted tetrazoles, the nature of the substituents present in the tetrazole ring was found to strongly affect the final products. However, as for the unsubstituted tetrazole, the main photoreaction path is either the molecular nitrogen elimination or the ring-cleavage [3+2] cycloelimination, leading to the production of azides.[21−27]

In view of the widespread interest in tetrazoles and allylic compounds, the photochemistry of the allylic derivatives of tetrazole is now under investigation in our laboratories. In the present work, we describe the photochemistry ($\lambda = 254$ nm) of 4-allyl-tetrazolones, **2a**−**c**, Figure 2, in solution. A mechanism of photocleavage for these tetrazolyl derivatives is proposed.

(6) Hashimoto, Y.; Ohashi, R.; Kurosawa, Y.; Minami, K.; Kaji, H.; Hayashida, K.; Narita, H.; Murata, S. *J. Cardiovasc. Pharmacol.* **1998**, *31*, 568.
(7) Desarro, A.; Ammendola, D.; Zappala, M.; Grasso, S.; Desarro, G. B. *Antimicrob. Agents Chemother.* **1995**, *39*, 232.
(8) Tamura, Y.; Watanabe, F.; Nakatani, T.; Yasui, K.; Fuji, M.; Komurasaki, T.; Tsuzuki, H.; Maekawa, R.; Yoshioka, T.; Kawada, K.; Sugita, K.; Ohtani, M. *J. Med. Chem.* **1998**, *41*, 640.
(9) Abell, A. D.; Foulds, G. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, *17*, 2475.
(10) Sandmann, G.; Schneider, C.; Boger, P. *Z. Naturforsch., C: Biosci.* **1996**, *51*, 534.
(11) Koldobskii, G. I.; Ostrovskii, V. A.; Poplavskii, V. S. *Khim. Geterotsikl. Soedin.* **1981**, *10*, 1299.
(12) Zhao-Xu, C.; Heming, X. *Int. J. Quantum Chem.* **2000**, *79*, 350.
(13) Araújo, N. C. P.; Brigas, A. F.; Cristiano, M. L. S.; Frija, L. M. T.; Guimarães, E. M. O.; Loureiro, R. M. S. *J. Mol. Catal. A: Chem.* **2004**, *215*, 113.
(14) Frija, L. M. T.; Cristiano, M. L. S.; Guimarães, E. M. O.; Martins, N. C.; Loureiro, R. M. S.; Bikley, J. *J. Mol. Catal. A: Chem.* **2005**, *242*, 241.
(15) Araújo, N. C. P.; Barroca, P. M. M.; Brigas, A. F.; Cristiano, M. L. S.; Johnstone, R. A. W.; Loureiro, R. M. S.; Pena, P. C. A. *J. Chem. Soc., Perkin Trans. 1* **2002**, *9*, 1213.
(16) (a) Kumar A.; Dittmer, D. C. *J. Org. Chem.* **1994**, *59* (9), 4760. (b) Adam, W.; Peters, K.; Reuz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1107. (c) Bergmeier, S. C.; Stanchina, D. M. *Tetrahedron Lett.* **1995**, *36*, 4533.
(17) Bugalho, S. C. S.; Lapinskii, L.; Cristiano, M. L. S.; Frija, L. M. T.; Fausto, R. *Vib. Spectrosc.* **2002**, *30*, 213.
(18) Cristiano, M. L. S.; Johnstone, R. A. W.; Price, P. J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1453.
(19) (a) Cristiano, M. L. S.; Johnstone, R. A. W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 489. (b) Cristiano, M. L. S.; Johnstone, R. A. W. *J. Chem. Res.* **1997**, 164.
(20) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie, GmbH: Weinheim, Germany, 1970. (b) Ito, H.; Taguchi, T. *Chem. Soc. Rev.* **1999**, *28*, 43. (c) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423. (d) Dessolin, M.; Eisenstein, O. K.; Golfier, M.; Prange, T.; Sautet, P. G. N. *J. Chem. Soc., Chem. Commun.* **1992**, 132. (e) Boudjabi, S.; Dewynter, G.; Montero, J. L. *Synlett* **2000**, *5*, 716. (f) Metz, P.; Mues, C.; Schoop, A. *Tetrahedron* **1992**, *48*, 1071.
(21) Dunkin, I. R.; Shields, C. J.; Quast, H. *Tetrahedron* **1989**, *45*, 259.
(22) Chae, Y. B.; Chang, K. S.; Kim, S. S. *Taehan Hwahakhoe Chi* **1967**, *11*, 85.
(23) Awadallah, A.; Kowski, K.; Rademacher, P. *J. Heterocycl. Chem.* **1997**, *34*, 113.
(24) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Phys. Chem. A* **2005**, *109*, 7967.
(25) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Mol. Struct.* **2005**, doi: 10.1016/j.molstruc.2005.08.019.
(26) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Photochem. Photobiol., A* **2005**, doi: 10.1016/j.jphotochem.2005.08.021.
(27) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L. S.; Fausto, R. *J. Photochem. Photobiol., A* **2005**, *179*, 243.

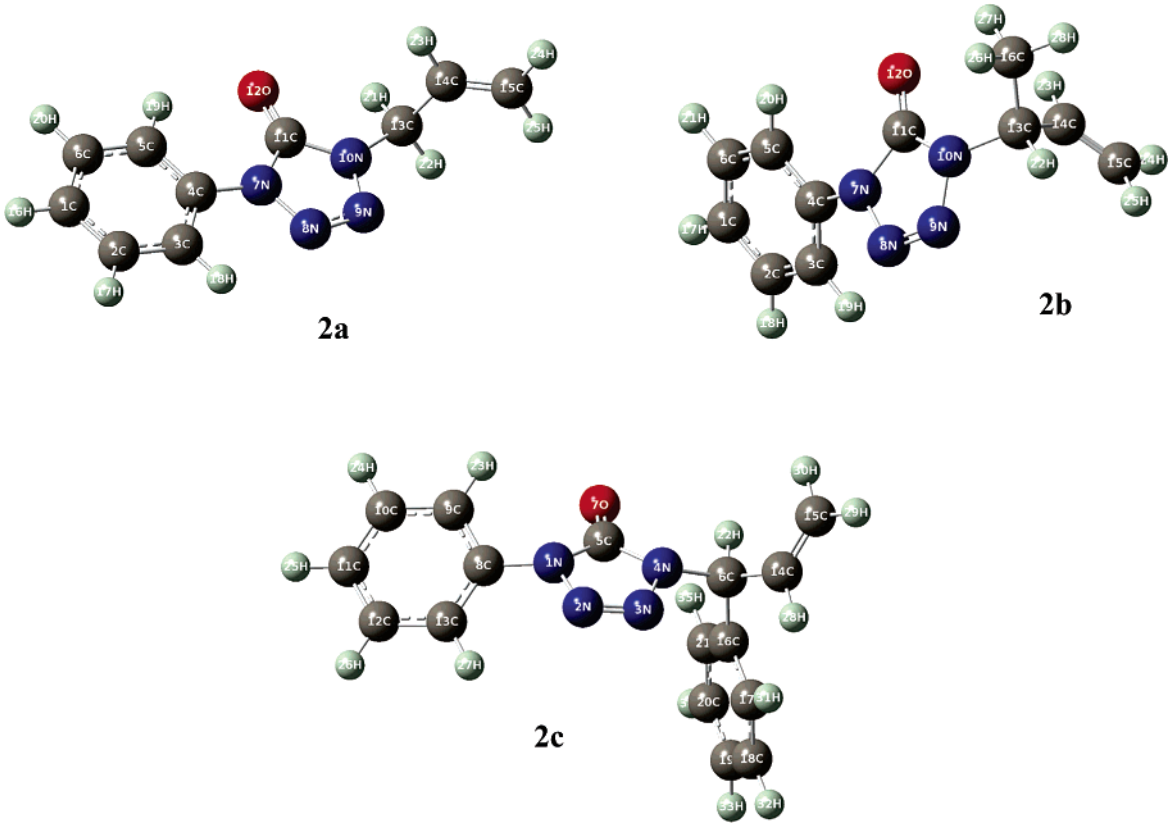


FIGURE 2. B3LYP/6-311G(d) optimized structures of 1-phenyl-4-(prop-2-enyl)-tetrazole-5-one (**2a**), 4-(1-methylprop-2-enyl)-tetrazole-5-one (**2b**), and 1-phenyl-4-(1-phenylprop-2-enyl)-tetrazole-5-one (**2c**) with the atom numbering. Tetrazolyl and phenyl rings are coplanar.

Results and Discussion

Compounds **2** are obtained from the corresponding tetrazolyl ethers **1** (Figure 1), with quantitative conversion, by heating a neat sample.[19a] Allyloxytetrazoles **1** were synthesized by the initial reaction of allylic alcohol with sodium hydride followed by the reaction with 5-chloro-1-aryltetrazole.

To assess the reaction mechanisms involved, two major aspects were addressed: (i) Structural elucidation of the photoproducts obtained after UV exposure ($\lambda = 254$ nm) of the tetrazolyl derivatives **2a**−**c** in methanol, 1-propanol, 1-hexanol, acetonitrile, and cyclohexane. (ii) Evaluation of structural effects, the nature of the solvent, and the effect of oxygen on the photoreactivity of compounds **2a**−**c**.

UV spectra of 4-allyl-tetrazolones **2a**−**c** show absorptions around 250 nm. These compounds were irradiated, and the progress of the photoreactions was monitored by HPLC. Quantum yields for photocleavage were determined separately. The results obtained are presented and discussed below.

Identification of the Photoproducts. Photolysis of 1-Phenyl-4-(prop-2-enyl)-tetrazole-5-one (2a). Photolysis of 4-allyl-tetrazolone **2a** was initially conducted in methanol. In all experimental conditions tested, namely, in air-equilibrated solutions, in solutions saturated with oxygen, or after purging with argon, a single photoproduct, identified as 3,4-dihydro-3-phenylpyrimidin-2(1*H*)-one **6a** (*m*/*z* = 174), was formed. Complete conversion of **2a** was observed after 65 min (Table 1). Extension of the irradiation time to 3 h did not modify the concentration of the primary photoproduct, and no signs of secondary photoproducts were registered.

Isolation of the photoproduct **6a** was carried out simply by solvent evaporation under reduced pressure in mild conditions (92%, isolated yield). The isolated dihydropyrimidinone **6a** is a stable compound, as no degradation was registered during storage. Interestingly, this molecule belongs to a novel structural class of pyrimidinones.[28]

TABLE 1. Evolution of Substrate Concentration[a] in the Photolysis[b] of 4-Allyl-tetrazolones 2a−c, Using Different Alcohols as Solvents

irradiation time (min)	substrate concentration (%)								
	methanol			1-propanol			1-hexanol		
	2a	**2b**	**2c**	**2a**	**2b**	**2c**	**2a**	**2b**	**2c**
0.25	93	92	94	95	96	97	98	98	99
0.50	90	89	91	92	94	95	95	95	97
1.0	87	87	89	89	92	92	92	91	95
2.0	83	81	84	85	89	90	88	87	92
4.0	74	75	78	78	84	85	82	84	89
8.0	56	61	62	64	75	78	75	77	85
12	43	49	52	53	65	67	68	67	80
20	32	38	41	40	51	55	56	57	71
40	14	19	23	21	36	40	41	44	61
60	3	6	8	10	17	26	29	32	53
90				3	5	14	23	26	45
120						5	17	20	37
150							10	13	31
180							3	7	23
210									15

[a] Relative yields determined by HPLC. [b] $\lambda = 254$ nm. Initial concentration of the substrates: 1.0×10^{-4} M.

The photoreactivity of 4-allyl-tetrazolone **2a** was also assessed in other alcohols. Irradiation of 4-allyl-tetrazolone **2a** in

(28) Frija, L. M. T.; Khmelinskii, I. V.; Cristiano, M. L. S. *Tetrahedron Lett.* **2005**, *46*, 6757.

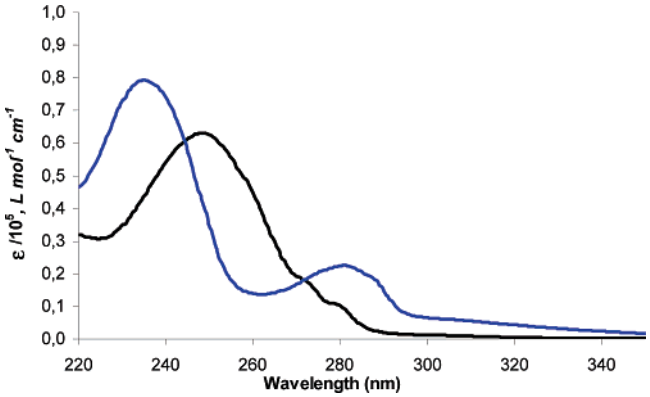


FIGURE 3. Extinction coefficients (ϵ) as a function of wavelength for tetrazolone **2a** (black line) and pyrimidinone **6a** (blue line) in methanolic solutions.

TABLE 2. Extinction Coefficient Values for Tetrazolones 2a−c and Pyrimidinones 6a−c Calculated at λ_{max}[a]

compound	λ_{max} (nm)	$\epsilon/10^5$ ($L \cdot mol^{-1} \cdot cm^{-1}$)
2a	249	0.63
2b	249	0.61
2c	250	0.89
6a	235	0.79
6b	233	0.69
6c	231	0.82

[a] Results obtained in methanol solution.

1-propanol and 1-hexanol also led to formation of 3,4-dihydro-3-phenylpyrimidin-2(1*H*)-one **6a** as the sole photoproduct. These results point to a single photochemical channel for the photodegradation of **2a** involving molecular nitrogen extrusion. The time for complete conversion of the substrate increased with the carbon chain length of the alcohol (65 min in methanol, 90 min in 1-propanol, and 190 min in 1-hexanol; Table 1).

Figure 3 shows the spectra of compounds **2a** and **6a**. Note that the primary product **6a** has some absorbance at the excitation wavelength and, thus, would reduce the apparent photolysis quantum yields at higher conversions, even in alcoholic solvents. The product interference becomes a more serious issue in nonalcoholic solvents, as the respective secondary photoproducts have even higher extinction coefficients. The extinction values for compounds **2a−c** and **6a−c** are given in Table 2. Note that the three starting compounds have similar extinction coefficients and positions of the peak maxima. The values of the extinction coefficients are typical for states of $\pi\pi^*$ nature.

The observed photoreactivity for tetrazolone **2a** in acetonitrile and cyclohexane was similar to that in alcohols, but the primary photoproduct **6a** was in turn photolyzed. In both solvents, three photoproducts were identified after irradiation: a primary photoproduct ($m/z = 174$) that coincides with the sole photoproduct obtained in alcoholic solutions, and two secondary photoproducts ($m/z = 93$ and 119). Analysis of the photolyzed samples taken every 2 s allowed for the identification of pyrimidinone **6a** as the primary photoproduct. The other (secondary) photoproducts started to be detectable at irradiation times exceeding 20 s and were identified as phenyl-isocyanate (**7**, $m/z = 119$) and aniline (**9**, $m/z = 93$) by comparing the HPLC and GC-MS traces with those of standard samples.

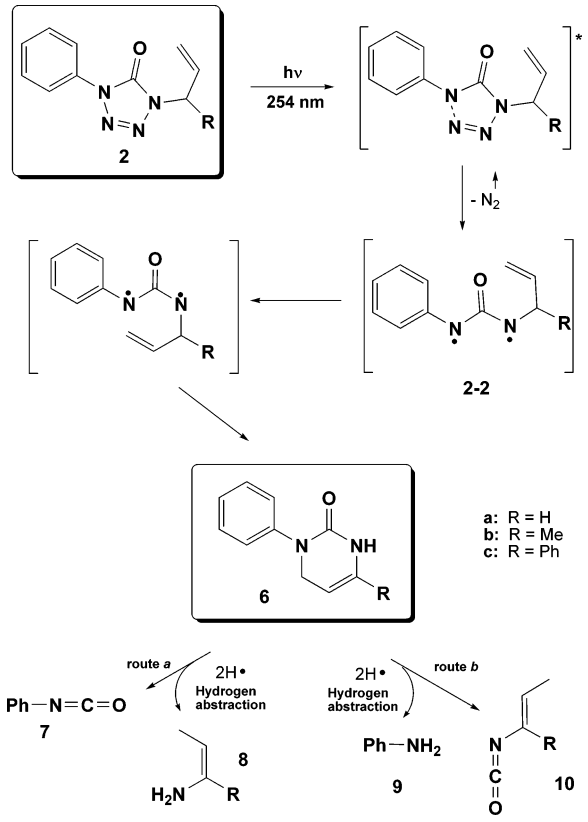


FIGURE 4. Proposed photodegradation pathways of 4-allyl-tetrazolones **2a−c** in solution.

A single mechanistic route is proposed for the formation of phenyl-isocyanate, involving the exclusive ring photocleavage of pyrimidinone **6a**, Figure 4, route ***a***. This mechanistic approach was confirmed when irradiation experiments using the pure pyrimidinone **6a** (isolated previously from the alcoholic solutions) were done in acetonitrile and cyclohexane. In the course of these experiments, formation of phenyl-isocyanate and aniline was detected, confirming that these two secondary photoproducts are a result of pyrimidinone photodegradation.

In contrast, two reactive channels could be possible for aniline formation: (i) photocleavage of the pyrimidinone ring to give directly the phenyl-nitrene (Ph−N:) intermediate, which will then abstract hydrogen from the solvent to form aniline and (ii) initial formation of phenyl-isocyanate that could undergo subsequent photocleavage to phenyl-nitrene, with elimination of CO, which would then abstract hydrogen to form aniline. However, in view of the experimental observations, we consider that aniline and phenyl-isocyanate are produced via two independent photochemical channels of degradation of pyrimidinone **6a**, Figure 4, routes ***a*** and ***b***.

Throughout the irradiation experiments, the appearance of these two compounds was detected at the same time, indicating that aniline is formed exclusively by photocleavage of the pyrimidinone ring and does not derive from phenyl-isocyanate. This hypothesis was confirmed by HPLC analysis of irradiated solutions of phenyl-isocyanate in acetonitrile and cyclohexane, in conditions similar to those used for allyltetrazolone **2a**. Phenyl-isocyanate remained photostable upon prolonged irradiation at 254 nm, and no aniline formation was ever detected.

The formation of phenyl-isocyanate and aniline by photocleavage of **6a** will be concomitant with the formation of two

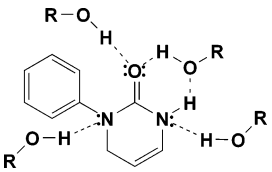


FIGURE 5. Solvation of pyrimidinone **6a** in alcoholic solutions.

other possible secondary products, 1-(amino) propene (**8a**) and 1-propenyl-isocyanate (**10a**), respectively. However, these photoproducts were never detected chromatographically throughout the irradiation experiments in any of the solvents. This could be explained by their high volatility, their fast photodecomposition into low molecular weight products, or their very rapid elution in the chromatographic conditions used.

The higher photostability of the primary photoproduct **6a** in alcohols against cyclohexane and acetonitrile can be explained based on solvent stabilization. In alcohols, there might be a strong association between the solvent and the photoproduct involving formation of relatively strong hydrogen bonds. Pyrimidinone **6a** bears several putative atoms capable of forming hydrogen bonds with solvent molecules, Figure 5. In such conditions, reversible proton transfer could be a fast and efficient mechanism of the excited-state quenching,[29] facilitated by steric limitations resulting from the stable cage enclosing the pyrimidinone molecule and preventing its photodecomposition. Also, the absorbed energy is more efficiently dissipated through the solvated complex, preventing relaxation through pathways leading to photocleavage.

^{1}H NMR spectra for compound **6a** were obtained in deuterated chloroform, acetonitrile, and methanol. In $CDCl_3$ and CD_3OD, all protons connected to carbon atoms show a similar chemical shift. However, in CD_3CN, the resonances for the same protons are shifted downfield by 0.25 to 0.35 ppm. The signal due to the resonance of the proton connected to the nitrogen (N−H) appears at 10.2 and 9.1 ppm in $CDCl_3$ and CD_3CN, respectively, and does not appear in CD_3OD.

Photolysis of 4-(1-Methylprop-2-enyl)-tetrazole-5-one (2b) and 1-Phenyl-4-(1-phenylprop-2-enyl)-tetrazole-5-one (2c). The photochemistry of 4-(1-methylprop-2-enyl)-tetrazole-5-one (**2b**) and 1-phenyl-4-(1-phenylprop-2-enyl)-tetrazole-5-one (**2c**) in solution was investigated using the methodology described above for tetrazolone **2a**. In methanol (air-equilibrated, oxygen-saturated, and argon-purged solutions), photolysis of these two tetrazolones resulted in the exclusive formation of the corresponding pyrimidinones **6b** and **6c** (Figure 4), identified as 3,4-dihydro-6-methyl-3-phenylpyrimidin-2(1*H*)-one (*m*/*z* = 188) and 3,4-dihydro-3,6-diphenylpyrimidin-2(1*H*)-one (*m*/*z* = 250), respectively. The same behavior was observed when using other alcohols. These pyrimidinones were isolated from the alcoholic solution in excellent yields (97% for **2b** and 90% for **2c**), and no evidence of secondary photoproducts was ever observed when extending the irradiation time. The time required for total photodegradation of 4-allyl-tetrazolones **2a**−**c** in the same alcohol varied for the three compounds (Table 1), increasing from R═H to R═CH_3 and then to R═Ph. As was noted for compound **2a**, the time required for complete conversion also increased with the viscosity of the alcohol.

The present investigation shows that the only photoproduct of **2a**−**c** formed in alcohols results from N_2 elimination from the tetrazolyl ring system through photoinduced cleavage of the weakest of the N−N formally single bonds ($N_{(7)}$−$N_{(8)}$ and $N_{(9)}$−$N_{(10)}$ for **2a**,**b**; $N_{(1)}$−$N_{(2)}$ and $N_{(3)}$−$N_{(4)}$ for **2c**), Figure 2, leading to the corresponding 3,4-dihydro-6-substituted 3-phenylpyrimidin-6-ones as sole products. Thus, this methodology represents a new synthetic strategy to these compounds, from 5-allylloxytetrazoles **1**, in excellent yields. Chemical diversity may be introduced easily by changing substituents in the allylic and the tetrazolic systems.[19,28]

In acetonitrile and cyclohexane, the photoreactivity of tetrazolones **2b**,**c** is also similar to that observed for **2a**. In these solvents, three photoproducts were identified for compound **2b**: a primary photoproduct (*m*/*z* = 188) coinciding with the sole photoproduct in methanol and two secondary photoproducts identified as phenyl-isocyanate (**7**, *m*/*z* = 119) and aniline (**9**, *m*/*z* = 93). The other possible secondary species formed via photodecomposition of **6b** are 2-amine-2-butene (**8b**) and 1-methylprop-1-enyl-isocyanate (**10b**), Figure 4. However, as for compounds **8a** and **10a**, these predicted photoproducts were never detected in any of the conditions tested during photolysis. Upon photolysis of tetrazolone **2c**, using the same solvents, four photoproducts were identified: the primary photoproduct (*m*/*z* = 250) that coincides with the sole photoproduct in methanol and three secondary photoproducts identified as phenyl-isocyanate (**7**, *m*/*z* = 119), aniline (**9**, *m*/*z* = 93), and 1-phenylprop-1-enyl-isocyanate (**10c**, *m*/*z* = 159), Figure 4.

Hence, the results obtained for the photolysis of compounds **2b**,**c** are analogous to those obtained for the photolysis of **2a**, unequivocally demonstrating that their photoreactivity is comparable and that substituent effects on the photoproduct distribution during the photolysis of the 4-allyl-tetrazolones in solution are negligible. However, as a result of an increase in the steric effects (it becomes more difficult for the fragments to separate with growing molecular size) from **2a** to **2c**, the time required for complete photodegradation of the three tetrazolones increases in the same order. As will be shown, similar conclusions follow from analysis of the quantum yield determinations.

Photoinduced loss of nitrogen from compounds **2a**−**c** may involve a cycloelimination leading to a diaziridinone that reacts further to give the observed 3,4-dihydro-6-substituted 3-phenylpyrimidin-2(1*H*)-ones **6a**−**c** or may occur through a biradical intermediate that subsequently cyclizes to give the same compounds **6a**−**c**. According to the literature, detection of biradical intermediates is not trivial and could not be achieved in this work. In several related investigations, such species were detectable only in a limited number of cases.[21] However, based on the experimental results obtained, it is our conviction that a radicalar mechanism operates in this case (Figure 4). Generally, the transition state in the concerted mechanism (cleavage of two N−N formally single bonds and formation of one new N−N formally single bond and the transformation of N═N double bond into N≡N triple bond) has a higher polarity as compared to that of the initial substrate. Considering the variation in polarity associated with the five solvents used in this work, it appears that the solvent polarity effects are weak or absent during tetrazolone photolysis, contrasting with what could be expected for a concerted process occurring via a polar transition state. No production of urea, via N_2 elimination followed by hydrogen abstraction, has ever been detected. However, this fact is not sufficient to discard the formation of a biradical intermediate in our experiments, because the reactive channel

(29) Solntsev, K. M.; Huppert, D.; Agmon, N.; Tolbert, L. M. *J. Phys. Chem. A* **2000**, *104*, 4658.

TABLE 3. Quantum Yields (λ = 254 nm, 25 °C) for the Photodegradation of 4-Allyl-tetrazolones 2a−c, in the Range of Solvents Used

solvent (air-eq.)	viscosity, η (mPa·s)	**2a**, Φ_{obs}	**2b**, Φ_{obs}	**2c**, Φ_{obs}
acetonitrile	0.37	0.38	0.35	0.31
methanol	0.54	0.36	0.34	0.30
cyclohexane	0.89	0.34	0.31	0.27
1-propanol	1.95	0.29	0.26	0.23
1-hexanol	4.58	0.23	0.20	0.17

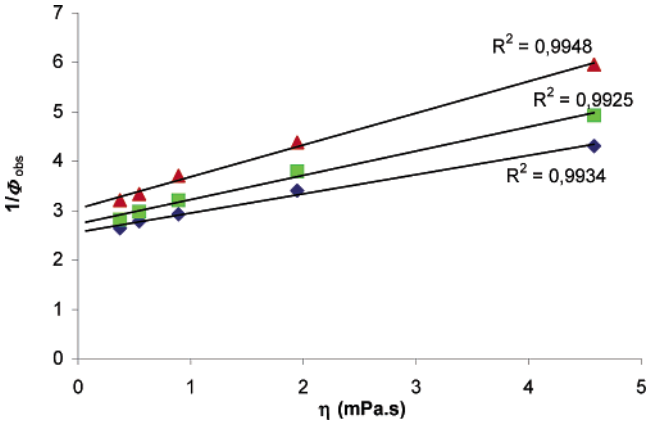


FIGURE 6. Plot of $1/\phi$ vs solvent viscosity (η) for the photolysis of 4-allyl-tetrazolones **2a** (◆), **2b** (■), and **2c** (▲) in argon-purged solutions. Values of viscosity at 25 °C: 0.369 (acetonitrile), 0.544 (methanol), 0.894 (cyclohexane), 1.945 (1-propanol), and 4.580 (1-hexanol) mPa·s.[30]

for radical recombination could be much more favorable than the hydrogen abstraction route.

Photolysis Quantum Yields and the Mechanism of Primary Reactions. The quantum yields obtained are rationalized on the basis of the following mechanism of primary reactions occurring upon photoexcitation of tetrazolones **2a−c**:

In Scheme 1, *Substrate* denotes the starting compound **2a−c**, *Product* denotes the reaction product **6a−c**, and [R^T···N_2*] denotes the caged radical pair, including the triplet biradical **2−2**. This reaction scheme is not quite complete, as it should additionally include re-encounters between R^T and N_2* that escaped the solvent cage and the reaction between R^T and O_2 in the bulk. However, the complete scheme would be too cumbersome for the analysis and unnecessary for the present purpose, given the lack of time-resolved kinetic data.

Because no fluorescence could be observed from the *Substrates*, we conclude that the reaction (2) is very fast and, consequently, the respective excited state formed in (1) and reacting in (2) is a singlet.

The Effect of Solvent Viscosity. Analysis of the results presented in Table 3 and Figure 6, obtained in argon-purged solutions, shows a direct correlation between the solvent viscosity[30] and the inverse photolysis quantum yield for tetrazolones **2a−c**. A good linear correlation is observed for the viscosity variations by 1 order of magnitude, with the photolysis quantum yields decreasing at higher viscosities. Considering the quantum yields obtained in the five solvents used in this work (Table 3), there is no apparent correlation between the photolysis quantum yields and the solvent dielectric constant. The conjugation of these results with the tetrazolone photoreactivity exhibited in the range of solvents used provides valuable information toward an interpretation of the mechanism that operates through the photolysis.

SCHEME 1

Substrate + *hν* → *Substrate**		(1)
*Substrate** → [R^T…N_2*]	ϕ_{pair}	(2)
[R^T…N_2*] → *Substrate*	k_r	
[R^T…N_2*] → [R^S…N_2]	k_{ST}	
[R^T…N_2*] + O_2 → [R^S…N_2] + O_2^*	k_q	
[R^S…N_2] → *Product* + N_2	*fast*	
[R^T…N_2*] → R^T + N_2*	k_d	
R^T → *Product*		

The observed viscosity dependence clearly points to the importance of the cage effect in the primary reaction mechanism.[31] We believe that the caged radical pair involving species **2−2** and N_2 (see Figure 4) is formed as the primary photoproduct, which may either recombine, reconstituting the parent molecule **2** (k_r) or escape from the cage (k_d), eventually yielding the photolysis product **6**. The importance of cage effects depends on the relative velocity (and, thus, the kinetic energy and the mass)[31] of the two fragments, as well as on the solvent viscosity.

Radical cage effects have an enormous impact on chemical reactivity in solution, and in fact, they are necessary to explain many fundamental reaction phenomena. These phenomena include rate−viscosity correlations, variations in products and product yields, and variations in quantum yields, as a function of medium. Expression (3) for the product quantum yield results from Scheme 1, in the absence of dissolved oxygen:

$$\phi = \phi_{pair}\frac{k_d + k_{ST}}{k_d + k_{ST} + k_r} \quad (3)$$

Considering $k_d = b/\eta$, we obtain:

$$\frac{1}{\phi} = \frac{1}{\phi_{pair}}\left(1 + \frac{k_r}{(b/\eta) + k_{ST}}\right) \quad (4)$$

Note that eq 4 is linear in η at sufficiently small values of η.

The value of ϕ_{pair} for each one of the three tetrazolones **2a−c** is obtained by extrapolating the plot of $1/\phi$ versus viscosity (Figure 6) to zero viscosity ($\phi_{pair,\mathbf{2a}} = 0.39$; $\phi_{pair,\mathbf{2b}} = 0.37$; $\phi_{pair,\mathbf{2c}} = 0.33$). The reduction of ϕ_{pair} with the size and molecular mass of the radicals should reflect the increasing probability of their re-encounters.[31]

As expected, the cage effect is increasing with viscosity. Thus, the cage effects can be used to explain the variations of the photolysis quantum yields as a function of medium for 4-allyl-tetrazolones **2a−c**.

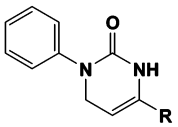
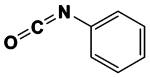
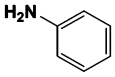
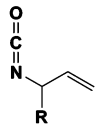
Effect of Oxygen on the Photoreactivity. It is well-known that, in the absence of low lying $^1(\pi,\pi^*)$ or charge transfer states, benzophenones show a high S_1 (n,π*) to T_1 (n,π*) intersystem crossing efficiency.[32] Considering the structure of tetrazolones **2a−c**, the presence of the carbonyl group in the tetrazole ring is possibly the main structural factor that could make it

(30) Lide, D. R., Ed. *CRC−Handbook of Chemistry and Physics*, version on CD-ROM; CRC Press: Boca Raton, FL, 2002.

(31) Braden, D. A.; Parrack, E. E.; Tyler, D. R. *Coord. Chem. Rev.* **2001**, *211*, 279.

(32) Turro, N. J. Photoaddition and photosubstitution reactions. In *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc.: San Francisco, CA, 1978; pp 362−413.

TABLE 4. Conversion of Substrate[a] and Product Distribution in the Photolysis[b] of 4-Allyl-tetrazolones 2a−c in Acetonitrile, Cyclohexane, and Methanol

Compound	Conditions	Substrate conversion (%)				 [c]
	CH_3CN (Ar-purged)	47	30	22	45	-
	CH_3CN (air-eq.)	84	26	20	52	-
	CH_3CN (O_2 sat.)	88	23	24	51	-
	Cyclohexane (Ar-purged)	34	29	31	37	-
2a	Cyclohexane (air-eq.)	66	31	29	37	-
	Cyclohexane (O_2 sat.)	71	31	26	40	-
	MeOH (Ar-purged)	48	96	-	-	-
	MeOH (air-eq.)	65	93	-	-	-
	MeOH (O_2 sat.)	78	95	-	-	-
	CH_3CN (Ar-purged)	48	21	32	41	-
	CH_3CN (air-eq.)	76	19	28	49	-
	CH_3CN (O_2 sat.)	79	20	28	45	-
	Cyclohexane (Ar-purged)	39	22	30	47	-
2b	Cyclohexane (air-eq.)	72	29	27	35	-
	Cyclohexane (O_2 sat.)	78	31	27	34	-
	MeOH (Ar-purged)	40	91	-	-	-
	MeOH (air-eq.)	73	92	-	-	-
	MeOH (O_2 sat.)	80	95	-	-	-
	CH_3CN (Ar-purged)	39	23	17	23	15
	CH_3CN (air-eq.)	70	17	24	21	14
	CH_3CN (O_2 sat.)	74	21	19	23	14
	Cyclohexane (Ar-purged)	36	31	14	24	19
2c	Cyclohexane (air-eq.)	56	21	17	30	23
	Cyclohexane (O_2 sat.)	69	25	19	24	20
	MeOH (Ar-purged)	39	92	-	-	-
	MeOH (air-eq.)	66	96	-	-	-
	MeOH (O_2 sat.)	70	95	-	-	-

[a] Relative yields in %, determined by HPLC. [b] Irradiation time, 20 min.; $\lambda = 254$ nm; concentration of substrate, 1.0×10^{-4} M. [c] **2a** (R = H), **2b** (R = CH_3), **2c** (R = Ph).

susceptible to photodegradation proceeding through the lowest triplet states. However, in the particular case of photolysis of compounds **2a−c**, we suppose that the reaction proceeds via a short-lived singlet excited state that quickly leads to a triplet biradical (Scheme 1, reactions 1 and 2).

Contrary to what should be expected for a triplet-mediated photoprocess, the presence of O_2, an efficient quencher of triplet states, was found to accelerate the photodegradation of tetrazolones in all of the tested solvents (see Table 4 for the photoconversion of substrates in Ar-purged, air-equilibrated, and O_2-saturated solutions).

One explanation for the increased photodegradation of **2a−c** in oxygen-saturated solutions could be the formation of an oxo-tetrazolone complex involving tetrazolone and O_2 molecules. This complex could reduce the influence of the solvent cage and increase photolysis quantum yields. In the oxygen/tetrazolone complex, the relevant HOMO and LUMO orbitals might also have a smaller energy difference, favoring nitrogen elimination. However, our attempts to detect the formation of such ground-state complexes in the UV spectra were fruitless. Another, more plausible explanation for the sensitizing effect of the molecular oxygen could be acceleration of the T−S conversion in the triplet biradicals, opening the way for the formation of the products **6a−c** and, consequently, improving the photolysis quantum yields (see the kinetic Scheme 1). The quantum yield as a function of oxygen concentration is given by expression (5), derived from the kinetic Scheme 1:

$$\phi = \phi_{pair}\frac{k_d + k_{ST} + k_q[O_2]}{k_d + k_{ST} + k_r + k_q[O_2]} \qquad (5)$$

where k_d is the first-order dissociation rate constant of the radical pair, k_r is its first-order recombination rate constant, k_{ST} is the intersystem conversion rate constant for the radical **2−2**, and k_q is its second-order reaction rate constant with dissolved oxygen. Figure 7 shows the product quantum yields in methanolic solutions for substances **2a−c** as a function of the oxygen concentration.

We may use the $k_q = 1 \times 10^{10}$ mol·L^{-1}·s^{-1}, equal to the diffusion-controlled reaction rate in methanol, thus obtaining an estimate $k_q[O_2] = 1 \times 10^8$ s^{-1} for the oxygen-induced S−T conversion rate at the highest oxygen concentrations used. The significant influence of the dissolved oxygen concentration on the product yields demonstrates that the rates of the other reactions in the Scheme 1 should be of comparable magnitude. However, presently, we are unable to obtain viable estimates

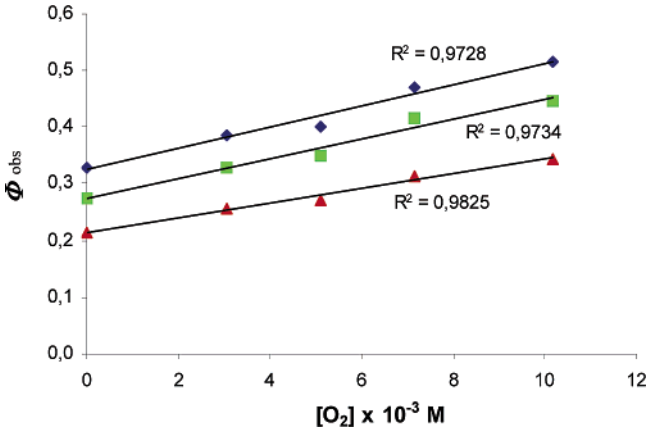


FIGURE 7. Plot of the product quantum yield as a function of oxygen concentration for 4-allyl-tetrazolones **2a** (◆), **2b** (■), and **2c** (▲) in methanolic solutions.

of the rates of the primary reactions without the results from time-resolved kinetic measurements, which we plan to perform soon.

Conclusion

Photolysis of the 4-allyl-tetrazolones **2a**−**c** in methanol, 1-propanol, and 1-hexanol solutions yields 3,4-dihydro-6-substituted-3-phenylpyrimidin-2(1*H*)-ones **6a**−**c** as sole products. These pyrimidinones are easily isolated from the alcoholic medium as stable compounds in excellent yields, providing an alternative and attractive synthetic methodology for this class of compounds. The observed photostability of pyrimidinones **6a**−**c** in alcohols is ascribed to a very efficient solvation, with formation of hydrogen bonds leading to deactivation of the excited state by reversible proton transfer, facilitated by stable solvent cages that enclose the pyrimidinone molecules and prevent their photodecomposition. The viscosity of the alcohols is directly related to the cage effects observed for 4-allyl-tetrazolones **2a**−**c**. Photoexcitation of 4-allyl-tetrazolones should involve formation of a caged triplet radical pair. This hypothesis is confirmed by the solvent viscosity effect on the photolysis quantum yields and the fact that the presence of dissolved oxygen accelerated photodegradation. The relative yields of all the identified photoproducts remained similar to those obtained in oxygenated, air-equilibrated and Ar-purged systems. The reaction appears to occur via a triplet biradical intermediate **2**−**2** with a lifetime of about 10^{-8} s. Pyrimidinones **6a**−**c** form additional photoproducts in solvents other than alcohols, where the effect of the solvent hydrogen bonds upon the reactivity of their excited state is negligible.

Experimental Section

Equipment. All chemicals were used as purchased. Solvents for extraction and chromatography were of technical grade. When required, solvents were freshly distilled from appropriate drying agents before use. Analytical TLC was performed with silica gel 60 F_{254} plates. Melting points are uncorrected. UV absorption spectra were recorded on a UV−visible spectrophotometer, using 1 × 1 cm quartz cells. Mass spectra were obtained on a mass spectrometer by electron ionization (EI) at 70 eV. ^{1}H NMR spectra were recorded in $CDCl_3$, CD_3OD, and CD_3CN (at 300 or 400 MHz) using TMS as an internal standard (δ = 0.0 ppm). Elemental analyses were performed on a standard elemental analyzer. Infrared spectra were registered in KBr disks.

HPLC analyses were performed using a chromatograph with a UV detector and a photodiode array. A column (RP-18, 5 μm) was used, and the runs were performed using a mixture of water and acetonitrile (40:60) as the eluent.

GC-MS analyses were carried out using a gas chromatograph with a series mass selective detector (EI, 70 eV), using a capillary column with 25 m length and 0.25 mm I.D. The initial temperature of 50 °C was maintained for 3 min and then a heating rate of 5 °C/min was applied until a final temperature of 250 °C was reached. Analyses were conducted on irradiated samples and on control solutions kept in darkness. Controls showed no sign of photodegradation.

Photodegradation studies were conducted in a reactor previously used to investigate the photochemistry of pesticides,[33] employing a merry-go-round and an immersion-well photochemical reactor immersed in water for cooling. The water temperature was kept constant (25 °C) using external circulation through a cooling bath. A 16-W low-pressure Hg lamp was used as source of the 254-nm UV radiation. Photolysis of tetrazolones **2a**−**c** was carried out in acetonitrile, cyclohexane, methanol, 1-propanol, and 1-hexanol, using 1-cm quartz cells at 10 to 40 cm from the lamp. Generally, 10^{-4} M starting solutions were used when the analysis was carried out by HPLC. More concentrated 10^{-2} M solutions were used for product identification using GC-MS.

Photolysis quantum yields were measured using the ferrioxalate actinometer.[34] A suitable interference filter was used to isolate the 254-nm line of the Hg lamp. Dissolved oxygen concentrations were varied by bubbling a controlled mixture of N_2 and O_2 through the solutions immediately before the photolysis for 10 min.

Preparation of 5-Allyloxytetrazoles. 1-Phenyl-5-(prop-2-enyloxy)-tetrazole (1a): prop-2-en-1-ol (allyl alcohol; 0.65 g; 11.1 mmol) in dry THF (10 mL) was added to a slurry of sodium hydride (55−60% in mineral oil; 0.72 g; 16.5 mmol) in dry THF (50 mL). The mixture was stirred at room temperature under an inert atmosphere until the effervescence ceased (20 min). 5-Chloro-1-phenyl-1*H*-tetrazole (2.0 g; 11.1 mmol) in dry THF (20 mL) was added, and the mixture was stirred overnight at room temperature. The reaction was monitored by TLC using a mixture of toluene/acetone (5:1) as eluent. Ice water (50 mL) was added, and the organic product was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated to dryness to give 1-phenyl-5-(prop-2-enyloxy)-tetrazole as a light yellow oil (1.8 g; 80% yield). IR ν_{max}: 1592, 1556, 1500, 1456, and 760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.10 (2H, d, J = 5.7 Hz), 5.30−5.60 (2H, m), 6.00−6.20 (1H, m), 7.40−7.60 (3H, m), 7.80 (2H, d, J = 6.9 Hz). Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.4; H, 5.0; N, 27.7%. Found: C, 59.2; H, 5.1; N, 28.2%. MS (EI): *m*/*z* 202 $[M]^+$.

Similarly, other allyloxytetrazoles were prepared.

1-Phenyl-5-[(*E*)-but-2-enyloxy]-tetrazole (1b): obtained from (*E*)-but-2-en-1-ol (crotyl alcohol; 1.0 g; 13.9 mmol) as light-yellow crystals (ethyl acetate, 67% yield), mp 36−37 °C. IR ν_{max}: 1597, 1560, 1505, 1448, and 761 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.75 (3H, d, J = 8.7 Hz), 5.05 (2H, d, J = 7.9 Hz), 5.72−5.90 (1H, m), 5.95−6.10 (1H, m), 7.40−7.65 (3H, m), 7.75 (2H, d, J = 8.3 Hz). Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%. Found: C, 61.1; H, 5.6; N, 26.0%. MS (EI): *m*/*z* 216 $[M]^+$.

1-Phenyl-5-[(E)-3-phenylprop-2-enyloxy]-tetrazole (1c): obtained from (*E*)-3-phenylprop-2-en-1-ol (cinnamyl alcohol; 0.8 g; 6.0 mmol) as colorless needles (ethyl acetate, 72% yield), mp 67−68 °C. IR ν_{max}: 1596, 1559, 1505, 1368, and 757 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.25 (2H, d, J = 7.0 Hz), 6.60 (1H, m), 6.85 (1H, d,

(33) Da Silva, J. P.; Da Silva, A. M.; Khmelinskii, I. V.; Martinho, J. M. G.; Vieira Ferreira, L. F. *J. Photochem. Photobiol., A* **2001**, *142*, 31.
(34) (a) Parker, C. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 104. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518. (c) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley and Sons: New York, 1967, pp 769−804.

J = 15.6 Hz), 7.24−7.80 (10H, m). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.9; H, 5.1; N, 20.2%. Found: C, 69.8; H, 5.0; N, 20.4%. MS (EI): *m*/*z* 278 $[M]^+$.

Preparation of 4-Allyl-tetrazolones. 1-Phenyl-4-(prop-2-enyl)-tetrazol-5-one (2a): 1-phenyl-5-(prop-2-enyloxy)-tetrazole (1.0 g; 4.9 mmol) was heated neat in an oil bath at 150 °C for 3 h to give the required 1-phenyl-4-(prop-2-enyl)-tetrazole-5-one as the sole product (quantitative yield). IR ν_{max}: 1729, 1598, 1504, 1388, and 757 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.65 (2H, d, J = 5.7 Hz), 5.35−5.52 (2H, m), 5.92−6.10 (1H, m), 7.40−7.60 (3H, m), 8.05 (2H, d, J = 6.86 Hz). Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.4; H, 5.0; N, 27.7%. Found: C, 59.8; H, 5.2; N, 28.1%. MS (EI): *m*/*z* 202 $[M]^+$.

4-(1-Methylprop-2-enyl)-tetrazol-5-one (2b): 1-phenyl-5-[(*E*)-but-2-enyloxy]-tetrazole (1.0 g; 4.6 mmol) was heated neat in an oil bath at 150 °C for 2 h to give 4-(1-methylprop-2-enyl)-tetrazole-5-one as the sole product (quantitative yield). IR ν_{max}: 1729, 1599, 1504, 1382, and 757 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.65 (3H, d, J = 5.7 Hz), 4.90−5.10 (1H, m), 5.22−5.40 (2H, m), 6.05−6.20 (1H, m), 7.30−7.55 (3H, m), 7.95 (2H, d, J = 8.6 Hz). Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.1; H, 5.6; N, 25.9%. Found: C, 61.0; H, 5.6; N, 26.1%. MS (EI): *m*/*z* 216 $[M]^+$.

1-Phenyl-4-(1-phenylprop-2-enyl)-tetrazol-5-one (2c): 1-phenyl-5-[(*E*)-3-phenylprop-2-enyloxy]-tetrazole (1.0 g; 3.6 mmol) was heated neat in an oil bath at 100 °C for 2 h to give 1-phenyl-4-(1-phenylprop-2-enyl)-tetrazole-5-one as the sole product (quantitative yield). IR ν_{max}: 1729, 1598, 1504, 1382, and 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.28−5.52 (2H, m), 6.00 (1H, d, J = 5.7 Hz), 6.36−6.55 (1H, m), 7.30−7.52 (8H, m), 7.95 (2 H, d, J = 8.6 Hz). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.1; H, 5.1; N, 20.1%. Found: C, 68.8; H, 5.0; N, 20.4%. MS (EI): *m*/*z* 278 $[M]^+$.

Preparation of Pyrimidinones. 3,4-Dihydro-3-phenylpyrimidin-2(1H)-one (6a): 1-phenyl-4-(prop-2-enyl)-tetrazole-5-one **2a** (0.10 g; 0.49 mmol) in methanol (50 mL) was irradiated at 254 nm in a photochemical reactor using a 16-W low-pressure Hg lamp. Photolysis was conducted at a distance of 10 cm from the lamp. Gas formation in the solution was observed, corresponding to the photoeliminated molecular nitrogen. HPLC analysis indicated total absence of initial reagent after 3 h. The solvent was evaporated under reduced pressure at room temperature to give 3,4-dihydro-3-phenylpyrimidin-2(1*H*)-one **6a** as a yellow oil (0.078 g; 92% isolated yield). IR ν_{max}: 3212 (NH), 3054, 1693 (C═O), 1590, 1566, 1496, 1368, 1230, 1059, and 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.65−4.68 (2H, d), 5.25−5.50 (1H, m), 7.12−7.20 (1H, m), 7.37−7.43 (3H, m), 7.50−7.57 (2H, t), 10.35 (1H, s). MS (EI): *m*/*z* 175 $[M + H]^+$. Accurate mass (CI): Anal. Calcd for $C_{10}H_{11}N_2O$, 175.12131; found, 175.12185.

Similarly, other pyrimidinones were prepared and isolated.

3,4-Dihydro-6-methyl-3-phenylpyrimidin-2(1*H*)-one (6b): from 4-(1-methylprop-2-enyl)-tetrazole-5-one **2b**, irradiated for 3.5 h, (97% isolated yield). IR ν_{max}: 3284 (NH), 3085, 1681 (C═O), 1598, 1548, 1484, 1446, 1378, 1230, 1068, and 755 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.58−1.62 (3H, s), 3.75−3.78 (2H, d), 5.22−5.30 (1H, m), 6.15−6.25 (1H, m), 7.05−7.17 (2H, m), 7.25−7.42 (2H, m), 10.20 (1H, s). MS (EI): *m*/*z* 189 $[M + H]^+$. Accurate mass (CI): Anal. Calcd for $C_{11}H_{13}N_2O$, 189.10280; found, 189.10299.

3,4-Dihydro-3,6-diphenylpyrimidin-2(1*H*)-one (6c): from 1-phenyl-4-(1-phenylprop-2-enyl)-tetrazole-5-one **2c** irradiated for 5 h (90% isolated yield). IR ν_{max}: 3220 (NH), 3066, 1701 (C═O), 1581, 1543, 1422, 1345, 1226, 1066, and 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.76−3.78 (2H, d), 5.42−5.48, (1H, m), 6.32−6.45 (1H, m), 6.70−6.75 (1H, m), 6.85−7.00 (2H, m), 7.10−7.35 (6H, m), 9.90 (1H, s). MS (EI): *m*/*z* 251 $[M + H]^+$. Accurate mass (CI): Anal. Calcd for $C_{16}H_{15}N_2O$, 251.11844; found, 251.11809.

Computational Details. The equilibrium geometries for the 4-allyl-tetrazolones **2a**−**c** were fully optimized at the DFT level of theory with the standard 6-311G(d) basis set, using the Gaussian 98 program.[35] DFT calculations were carried out with the three-parameter density functional, abbreviated as B3LYP, which includes Becke's gradient exchange correction[36] and the Lee, Yang, and Parr correlation functional.[37] No symmetry restrictions were imposed on the initial structures. Atom numbering schemes for the molecules studied are given in Figure 2.

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Supporting Information Available: Optimized geometries and absolute energies for the 4-allyl-tetrazolones are available in Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(36) Becke, A. D. *Phys. Rev. B: Condens. Matter* **1988**, *38*, 3098.

(37) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.