

Article

# Reinvestigation of the Room Temperature Photochemical Reaction between *N*-Methyl-1,2,4-triazoline-3,5-dione (MeTAD) and Benzene

 Gary W. Breton 

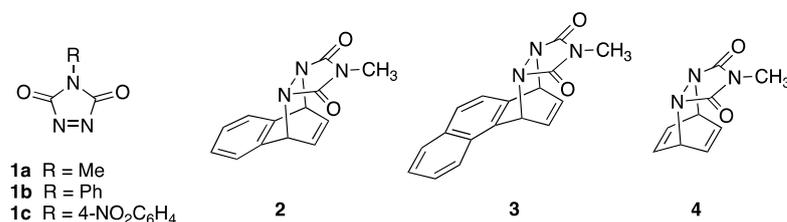
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**Abstract:** The photochemical reaction of *N*-methyl-1,2,4-triazoline-3,5-dione (MeTAD) with benzene is known to lead to a Diels–Alder cycloaddition product when conducted at low temperatures (i.e.,  $<-60$  °C). This reactivity has been exploited recently for novel synthetic applications. It was previously reported that no reaction between MeTAD and benzene occurs at room temperature. However, it has now been discovered that MeTAD reacts effectively with benzene upon visible light irradiation over a several day period at room temperature. The major product is a *para*-substituted bisurazole adduct. Our studies indicate that the adduct is formed via sequential aromatic substitution reactions made possible by electron transfer from the aromatic ring to the highly electrophilic triplet state of photoactivated MeTAD.

**Keywords:** *N*-methyl-1,2,4-triazoline-3,5-dione; MeTAD; Diels–Alder; benzene; photochemistry

## 1. Introduction

*N*-Substituted 1,2,4-triazoline-3,5-diones (TADs, **1**, see Figure 1) are highly electrophilic azo compounds that undergo thermal reactions with many classes of organic compounds, including alcohols, alkenes, alkynes, and aromatic substrates [1]. TADs are generally deep red in color, rendering them susceptible to further activation via visible-light irradiation [2]. Indeed, under photochemical conditions, the reactivity of TADs is known to be even further enhanced, allowing for many reactions that will not occur thermally, as for example, reaction with strained saturated C–C bonds and aromatic substrates [2–4].



**Figure 1.** Structure of triazolinedione compounds **1a–c**, and the cycloadducts formed via the photochemical reaction of **1a** with naphthalene (**2**), phenanthrene (**3**), and benzene (**4**).

In a series of seminal papers, Sheridan demonstrated that *N*-methyl-1,2,4-triazoline-3,5-dione (MeTAD, **1a**) undergoes photochemical Diels–Alder (DA) type cycloaddition reactions with naphthalene, phenanthrene, and even benzene, to form cycloadducts **2**, **3**, and **4**, respectively [5–8]. While further studies in our lab demonstrated that naphthalene exhibited some thermal reactivity with **1a** to form **2** [9], photochemical conditions drove the reaction to completion faster, and provided a higher isolated yield. On the contrary, however, no reaction between **1a** and either phenanthrene or benzene is observed in the absence of light [7,8]. In addition, whereas reaction with naphthalene and phenanthrene



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occurs at room temperature, the photochemical reaction with benzene was reported to take place only at temperatures below  $-60\text{ }^{\circ}\text{C}$ , and no reaction at room temperature [5,8].

The photochemically driven Diels–Alder reaction of **1a** with benzene is of particular significance given the general reluctance of benzene to undergo any sort of addition reaction because of the resulting loss of aromatic stabilization, although exceptions have been noted [10]. Wamhoff first recorded the ability to engage benzene in photoreactivity with a triazolinedione (using the especially electrophilic *N*-4-nitrophenyl derivative, **1c**) in 1977 [2]. Sheridan’s work more clearly documented the course of such reactions in 1989 [8]. More recently, Sarlah’s group (2016–current) has exploited the photo-driven Diels–Alder reactivity of aromatics with MeTAD for fascinating synthetic applications [11,12].

Given the recent resurgence in both the interest and applications of this reaction, in this report, a related finding is described in which a novel adduct resulting from a double electrophilic aromatic substitution reaction was observed during the photochemical reaction of **1a** with benzene at room temperature.

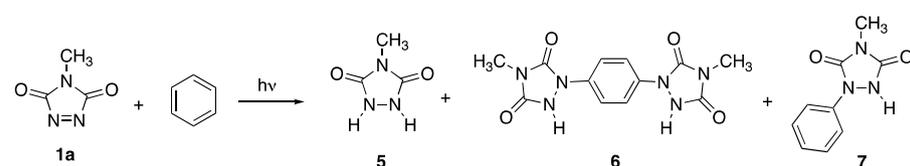
## 2. Results

During the course of a previous study on the room temperature photochemical reactions of **1a** with variously substituted benzenes [4], a reinvestigation of the reaction of **1a** with benzene was undertaken. The results of these reactions are summarized in Table 1. Thus, within 3 h of visible light ( $3 \times 300\text{ W}$  incandescent bulbs) irradiation of 10 mL of a red-colored solution of **1a** and benzene (0.1 M each) in  $\text{CH}_2\text{Cl}_2$ , some crystals were observed to form on the sides of the reaction vessel. After irradiating for a total of 24 h, the crystals needed to be scraped from the sides and allowed to settle to the bottom of the reaction flask, in order to admit sufficient light to continue the photochemical reaction. After 48 h of irradiation, additional crystals formed, and the solution turned to a very pale pink color, indicating the near complete consumption of **1a**. The crystals were isolated via vacuum filtration. Analysis of the crystals by  $^1\text{H}$  NMR spectroscopy indicated the presence of a ~2:1 mixture of *N*-methylurazole **5** (Scheme 1) and an additional novel compound. This novel compound was insoluble in methanol (whereas **5** has appreciable solubility) so separation of the two compounds proved to be operatively simple. It was calculated that 30% of **1a** had been converted to **5** (Table 1, entry 1).

**Table 1.** Effect of reaction conditions on yields of products **5**, **6**, and **7**.

Entry	Solvent	Equivalents Benzene <sup>1</sup>	Time (h)	% Yield <b>5</b>	% Yield <b>6</b>	% Yield <b>7</b>
1	$\text{CH}_2\text{Cl}_2$	1	48	30	17	<5
2	$\text{CH}_2\text{Cl}_2$	5	>48 h	13	7	<5
3	$\text{CH}_3\text{CN}$	1	72	0	53	<10
4	$\text{CH}_3\text{CN}$	1	24 <sup>2</sup>	0	16	10

<sup>1</sup> Equivalents of benzene added relative to MeTAD (**1a**), <sup>2</sup> reaction stopped prior to completion.



**Scheme 1.** Reaction of MeTAD (**1a**) with benzene to afford *N*-methylurazole **5**, bisurazole adduct **6**, and monosubstituted urazole **7**.

Analysis of the novel compound by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and HRMS revealed the structure to be that of the *para*-substituted bisurazole compound **6** (see spectra provided in the Supplementary Materials). Only a single *N*-methyl signal was observed in the  $^1\text{H}$  NMR spectrum, but that would be consistent with the *ortho*- and *meta*-substituted products as well, due to the symmetry of the various possible regioisomers. However, only a single

singlet was observed for all four of the aromatic protons in the  $^1\text{H}$  NMR spectrum, and only two carbon signals for the six benzene ring carbons in the  $^{13}\text{C}$  NMR spectrum. These data are only consistent with the *para*-substituted structure of **6**. This compound was formed in 17% yield (Table 1, entry 1).

Concentration of the filtrate from above, and examination of its contents by  $^1\text{H}$  NMR spectroscopy revealed the presence of photodegradation products of **1a**, and trace amounts of the known monosubstituted urazole **7**. Such photodegradation of TADs in solution has been documented before [2,13]. It should be noted that Wamhoff had reported the formation of a monosubstituted urazole comparable to **7** upon irradiation of **1c** with benzene [2]. He did not, however, observe the formation of a bis-adduct.

In an attempt to increase the rate of reaction, the amount of benzene in the reaction was increased to five equivalents relative to **1a**, but under otherwise identical conditions (see Table 1, entry 2). Interestingly, the reaction proceeded even slower in the presence of excess benzene, and the solution remained deep purple-red in color even after 2 days of irradiation. Furthermore, the combined yield of **5** and **6** isolated as crystals (26 mg) was less than that when equimolar amounts of the two starting materials had been irradiated (60 mg). Concentration of the remaining filtrate afforded unreacted MeTAD, small amounts of **7**, and photodegradation products.

It was suspected that the *N*-methylurazole **5** that was formed might be a result of the reaction of photoactive **1a** with  $\text{CH}_2\text{Cl}_2$  with the solvent acting as an H-donor. Therefore, the solvent was changed to  $\text{CH}_3\text{CN}$  and the reaction was then carried out under otherwise identical conditions (Table 1, entry 3). The reaction took 3 days to complete, as opposed to the 2 days in  $\text{CH}_2\text{Cl}_2$ , but the only product observed was bisurazole **6** and in a higher isolated yield of 53%. Concentration of the filtrate revealed the presence of small amounts (<10%) of monosubstituted **7** in addition to photodegradation products. Next, a control reaction was carried out for a period of only 24 h such that the reaction was intentionally not allowed to run to completion (Table 1, entry 4). Under these conditions, bis-adduct **6** was isolated in 16% yield and monosubstituted **7** was obtained in 10% yield.

As a control experiment to definitively determine that bisurazole **6** was formed from further reaction of monosubstituted **7**, MeTAD was irradiated in 10 mL of a saturated acetonitrile solution of **7**, but otherwise in the absence of any added benzene. As before, crystal formation was observed to take place within a few hours of irradiation. After 24 h, bis-adduct **6** was isolated in 65% yield, confirming that final product **6** is formed via initially generated **7**.

Finally, it is interesting to note that an attempt to carry out this reaction with the *N*-phenyl TAD derivative PhTAD (**1b**) in  $\text{CH}_3\text{CN}$  did not lead to the formation of either mono or disubstituted adducts even after carrying out the irradiation for a total of 4 days. Indeed, at least 80% of **1b** remained present in solution at the end of the reaction period.

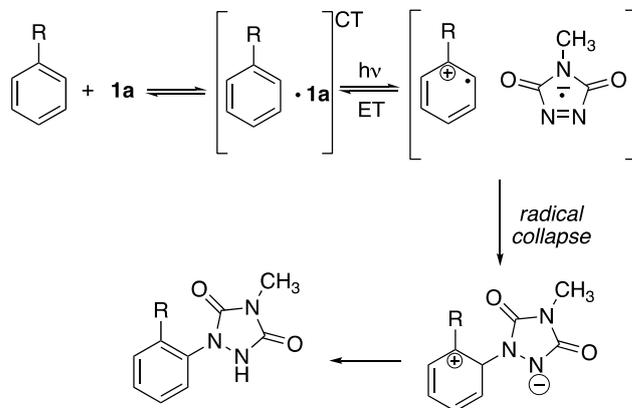
### 3. Discussion

During initial studies of the photochemical reaction of MeTAD with various aromatic compounds (presumably at room temperature), Sheridan reported that his group was unable to observe any reaction with benzene or several substituted benzenes [5]. However, he reported that successful Diels–Alder reactivity with benzene to form **4** was readily observed when the photochemical reaction was conducted at temperatures below  $-60\text{ }^\circ\text{C}$  (in benzene as solvent) [8]. Raising the temperature to even  $-10\text{ }^\circ\text{C}$  was sufficient to trigger a retro-Diels–Alder reaction to occur, converting the cycloadduct back to starting materials ( $t_{1/2} = 1\text{ h}$  at  $0\text{ }^\circ\text{C}$ ). The lack of observed reactivity at room temperature, therefore, could be explained by the thermal instability of the cycloadduct. In other words, although photochemical cycloaddition actually occurred at room temperature to form **4**, the cycloaddition product quickly reverted to starting materials via the thermally driven retro-DA process, thereby providing an illusion of no reaction. Therefore, it was fortunate that under the experimental conditions of this study, the beginnings of crystal formation on the sides of

the reaction vessel had been observed, because formation of these crystals prompted the continued irradiation of the solution for an extended period of time.

It is interesting that even when the photochemical reaction conducted in  $\text{CH}_3\text{CN}$  was interrupted prior to the complete consumption of **1a** (Table 1, entry 4), the amount of disubstituted product **6** was in excess of the monosubstituted **7**. The preference for the formation of **6** was also the case for the reaction conducted in  $\text{CH}_2\text{Cl}_2$  in the presence of an excess of benzene. Such conditions might be expected to favor the formation of the monosubstituted adduct over the disubstituted adduct. Therefore, monosubstituted **7** must be more reactive toward photoactivated **1a** than benzene itself. This behavior is consistent with the urazole ring acting as an activating (electron-donating) substituent on the ring.

In our earlier studies on the photochemical reactions of **1a** with substituted benzenes [4], it was concluded that reaction occurred upon the irradiation of an initially formed charge transfer (CT) complex between the arene and **1a** (see Scheme 2). Irradiation promoted a single electron transfer from the benzene ring **1a**, resulting in the formation of a radical cation from the aromatic substrate and a radical anion from **1a**. These newly formed radicals collapsed to form a bond, thereby giving rise to the sigma complex characteristic of traditional electrophilic aromatic substitutions. Finally, proton transfer afforded the final substituted product. This electron-transfer process was promoted by the presence of electron-donating substituents on the aromatic ring. While the electron-transfer process was energetically favorable for the electron-rich substrates investigated earlier, electron transfer from unsubstituted benzene to the singlet excited state of **1a** (i.e.,  $^1\mathbf{1a}^*$ ) is energetically disfavored. Previous estimates suggested that this process may be endothermic by as much as 15 kcal/mol [8]. Sheridan suggested that while  $^1\mathbf{1a}^*$  was certainly involved in the photochemical Diels–Alder reaction of **1a** with benzene to form **4**, the involvement of the corresponding triplet state (i.e.,  $^3\mathbf{1a}^*$ ) in this cycloaddition process remained unclear.

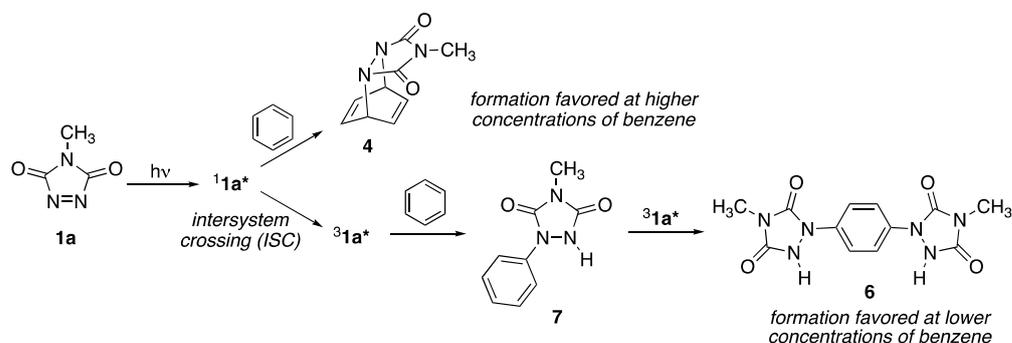


**Scheme 2.** Mechanism for the photochemical reaction of MeTAD (**1a**) with aromatic substrates to form substituted products.

Chattaraj recently postulated that the “global electrophilicity index” of molecules, a measure of a compound’s willingness to react as an electrophile, is increased upon electronic excitation [14]. Using the identical computational protocol as Chattaraj (i.e., TDDFT B3LYP/6-311+G\*\*), a global electrophilicity index was calculated for the ground state of **1a** to be 2.18 eV, a comparably equivalent electrophilicity index of 2.09 eV was calculated for the excited singlet state  $^1\mathbf{1a}^*$ , and a substantially increased electrophilicity index of 3.56 eV for the excited triplet state,  $^3\mathbf{1a}^*$ . Thus, electron transfer from benzene to photoexcited **1a**\*, while apparently not feasible from the singlet excited state, may be favorable from the triplet excited state.

The triplet state of **1a**\* is populated via intersystem crossing (ISC) from the initially generated singlet state (see Scheme 3). If, however, the singlet state is effectively quenched by reaction with benzene in a Diels–Alder cycloaddition process, there is little opportunity for the population of the triplet state. At lower concentrations of benzene, one might then

expect greater opportunity for the population of the triplet state, which could then undergo reaction with benzene via an electron-transfer process. With increasing concentrations of benzene (as, for example, increasing the amount of benzene from 1 to 5 equivalents as was discussed above) one would, therefore, expect a decreased rate of reaction to form 6/7 since more of the singlet excited state of benzene would be effectively trapped (and then replenished via the thermal retro-Diels–Alder reaction), as was experimentally observed.



**Scheme 3.** Proposed reaction pathway for the photochemical reaction between MeTAD (**1a**) and benzene to form observed products **4**, **6**, and **7**.

Finally, electron transfer from monosubstituted **7** to  $^3\mathbf{1a}^*$  to give rise to **6** should be favored relative to the electron transfer from benzene itself because the attached urazole ring acts as an electron-donating substituent, and promotes greater reactivity.

#### 4. Conclusions

Contrary to earlier reports that suggested that there was no photochemical reaction between **1a** and benzene at room temperature, it was found that they do, indeed, react. While Diels–Alder cycloadduct **4** is the product of the reaction at low temperatures ( $<60\text{ }^\circ\text{C}$ ), a bisurazole adduct **6** is the major product at room temperature. This discrepancy in observations is traced to the rapid thermal retro-Diels–Alder reaction of **4** at room temperature, which may provide an illusion of no reaction. Furthermore, while the Diels–Alder cycloaddition process takes place from the singlet state of photoactivated **1a**, the electron-transfer process that leads to compounds **6/7** may take place from the triplet activated state. In the presence of higher concentrations of benzene, the cycloaddition process dominates, thereby quenching the excited state and preventing population of the triplet state  $^3\mathbf{1a}^*$  via intersystem crossing. With lower concentrations of benzene, the rate of reaction via the Diels–Alder cycloaddition is decreased, and population of  $^3\mathbf{1a}^*$  is made possible. Under these conditions, electron-transfer from benzene to the electrophilic  $^3\mathbf{1a}^*$  occurs, leading to the formation of **7**. Because the urazole ring of **7** acts as an electron-donating substituent, the rate of reaction of **7** with  $^3\mathbf{1a}^*$  to form **6** is enhanced, and final yields of **6** consistently surpass those of **7**.

Finally, it is of importance to note that this observed photochemical reactivity of MeTAD with benzene, and substituted benzenes [4], conforms with some of the twelve principles previously laid out for Green Chemistry [15]. From the standpoint of atom economy, especially when these reactions are carried out in  $\text{CH}_3\text{CN}$  as solvent during which no formation of the side-product **5** was observed, a maximum number of atoms of the starting materials are incorporated into the product. Additionally, the ability to conduct these reactions under an oxygen atmosphere at room temperature conforms to the principle of designing a reaction for energy efficiency.

#### 5. Materials and Methods

##### 5.1. General Methods

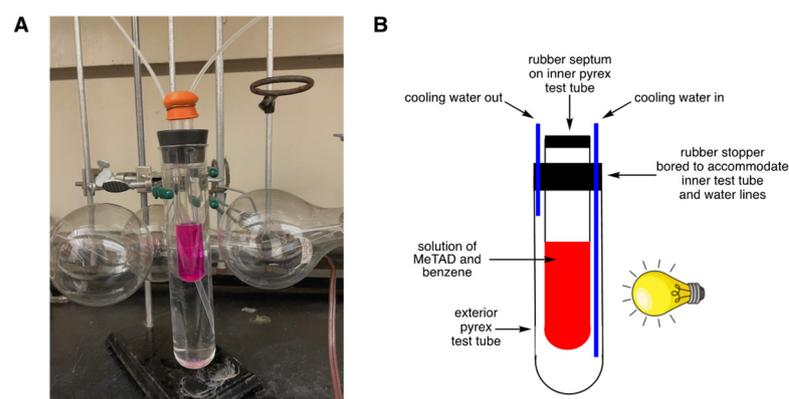
Chemical shifts are reported in units of parts per million downfield from TMS. High-resolution mass spectra (HRMS) were acquired via electron spray ionization on an LTQ-

FTMS hybrid mass spectrometer. *N*-Methyl-1,3,5-triazoline-3,5-dione (MeTAD) was synthesized via oxidation of *N*-methylurazole with DABCO-Br<sub>2</sub> as described in the literature [16,17]. Compound **7** was prepared according to the literature [18]. All other reagents were commercially obtained and used as received. All photochemical reactions were conducted under an atmosphere of air.

## 5.2. Experimental Procedures

### 5.2.1. Photochemical Reaction of MeTAD (**1a**) with One Equivalent of Benzene in CH<sub>2</sub>Cl<sub>2</sub>

To a clear red solution of 113 mg (1 mmol) of **1a** in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> in a Pyrex test tube, 90  $\mu$ L (1 equiv) of benzene was added via syringe. The test tube was sealed with a rubber septum and placed into a water-jacketed apparatus made from a larger Pyrex test tube as shown in Figure 2. The water-cooled solution was irradiated with three 300 W incandescent bulbs arranged around the outside Pyrex test tube less than a cm from the exterior of the test tube wall. Within 3 h of irradiation, some crystal formation was noted on the wall of the interior test tube. After irradiating for 24 h, the septum sealing the interior test tube was removed, and the crystals that had collected on the wall of the interior test tube were scraped as much as possible and allowed to settle at the bottom of the test tube where they would not inhibit incoming light. The remaining solution remained deep purple/red in color. After 48 h of irradiation, the solution was a very pale pink in color. The crystals were isolated via vacuum filtration to afford 60 mg of crude product that proved to be a mixture of compounds **5** and **6** by <sup>1</sup>H NMR spectroscopy. This mixture of compounds was heated in 2 mL CH<sub>3</sub>OH and filtered to afford 26 mg (17% yield) of **6** as a white solid. Concentration of the CH<sub>3</sub>OH afforded 34 mg (30% yield) of **5** as a white solid. Finally, the reaction filtrate from whence the crystal mixture was derived was concentrated in vacuo to a pink foam. Analysis of this foam by <sup>1</sup>H NMR showed benzene, small amounts of unreacted **1a**, uncharacterized photodegradation products, and traces of **7** (identified by comparison of <sup>1</sup>H NMR and IR data to that provided in the literature, [16]). For 4-methyl-1-[4-(4-methyl-3,5-dioxo-1,2,4-triazolidin-1-yl)phenyl]-1,2,4-triazolidine-3,5-dione (**6**): white solid, m.p. > 300 °C; IR (ATR) cm<sup>-1</sup> 3122, 1774, 1693, 1520, 1479, 1333, 1006, 811; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  11.12 (br s, 2H), 7.60 (s, 4H), 2.97 (s, 6H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>)  $\delta$  153.7, 150.9, 133.5, 118.9, 25.0; and HRMS (ESI) m/z [M+H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>13</sub>N<sub>6</sub>O<sub>4</sub> 305.0993; Found 305.0991.



**Figure 2.** (A) An image of the photochemical apparatus set-up as actually deployed in the lab (lights are off). (B) A schematic describing the components.

### 5.2.2. Photochemical Reaction of MeTAD (**1a**) with Five Equivalents of Benzene in CH<sub>2</sub>Cl<sub>2</sub>

To a clear red solution of 113 mg (1 mmol) of **1a** in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> in a Pyrex test tube, 450  $\mu$ L (5 equivalents) of benzene was added via syringe. The test tube was sealed with a rubber septum and placed in a water-jacketed apparatus made from a larger Pyrex test tube as shown in Figure 2. The water-cooled solution was irradiated with three 300 W incandescent bulbs arranged around the outside Pyrex test tube less than a cm from the

exterior of the test tube wall. After irradiating for 24 h, the septum sealing the interior test tube was removed, and the crystals that had collected on the wall of the interior test tube were scraped as much as possible and allowed to settle at the bottom of the test tube where they would not inhibit the incoming light. After 48 h of irradiation, the solution remained deep purple/red in color, indicating incomplete consumption of **1a**. The crystals were isolated via vacuum filtration to afford 26 mg of crude product that proved to be a mixture of compounds **6** and **7** by  $^1\text{H}$  NMR spectroscopy. The reaction filtrate was concentrated in vacuo to a viscous red liquid. Addition of 5 mL of  $\text{CH}_2\text{Cl}_2$  to this liquid resulted in the precipitation of a solid that was collected via vacuum filtration (12 mg). Analysis of this solid by  $^1\text{H}$  NMR spectroscopy revealed it to consist of mostly monosubstituted urazole **7** and a small amount of urazole **5**.

### 5.2.3. Photochemical Reaction of MeTAD (**1a**) with One Equivalent of Benzene in $\text{CH}_3\text{CN}$

To a clear red solution of 113 mg (1 mmol) of **1a** in 10 mL of anhydrous  $\text{CH}_3\text{CN}$  in a Pyrex test tube, 90  $\mu\text{L}$  (1 equivalent) of benzene was added via syringe. The test tube was sealed with a rubber septum and placed in a water-jacketed apparatus made from a larger Pyrex test tube as shown in Figure 2. The water-cooled solution was irradiated with three 300 W incandescent bulbs arranged around the outside Pyrex test tube less than a cm from the exterior of the test tube wall. After irradiating for 24 h, the septum sealing the interior test tube was removed, and the crystals that had collected on the wall of the interior test tube were scraped as much as possible and allowed to settle at the bottom of the test tube where they would not inhibit incoming light. The solution remained deep purple/red in color. This process was repeated after 48 h of irradiation. After 72 h of irradiation, the solution was very pale pink in color. The crystals were isolated via vacuum filtration to afford 80 mg (53% yield) of **6**.

### 5.2.4. Photochemical Reaction of MeTAD (**1a**) with One Equivalent of Benzene in $\text{CH}_3\text{CN}$ Stopped Prior to Reaction Completion

To a clear red solution of 113 mg (1 mmol) of **1a** in 10 mL of  $\text{CH}_3\text{CN}$  in a Pyrex test tube, 90  $\mu\text{L}$  (1 equivalent) of benzene was added via syringe. The test tube was sealed with a rubber septum and placed into a water-jacketed apparatus made from a larger Pyrex test tube as shown in Figure 2. The water-cooled solution was irradiated with three 300 W incandescent bulbs arranged around the outside of the Pyrex test tube less than a cm from the exterior of the test tube wall. Within 3 h of irradiation, some crystal formation was noted on the wall of the interior test tube. After irradiating for 24 h, crystals had formed on the wall of the interior test tube and the solution remained deep purple/red in color. The crystals were isolated via vacuum filtration to afford 24 mg (16% yield) of **6**. The deep red-colored filtrate was treated dropwise with a solution of 2,3-dimethyl-1,3-butadiene in  $\text{CH}_3\text{CN}$  until the red color of the **1a** was completely discharged. The resulting colorless solution was concentrated in vacuo and taken up in 10 mL of  $\text{CH}_2\text{Cl}_2$ . This organic layer was extracted with  $1 \times 10$  mL 0.5 M aq. NaOH. The aqueous layer was acidified to pH  $\sim 2$  and extracted with  $3 \times 5$  mL of  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to afford 19 mg (10% yield) of **7**.

### 5.2.5. Photochemical Reaction of MeTAD (**1a**) with **7** in $\text{CH}_3\text{CN}$

To a solution of 15 mg ( $2.85 \times 10^{-5}$  mol) of **7** [18] in 10 mL of  $\text{CH}_3\text{CN}$  in a Pyrex test tube, 0.113 g (1 mmol) of MeTAD was added. The test tube was sealed with a rubber septum and placed in a water-jacketed apparatus made from a larger Pyrex test tube as shown in Figure 2. The water-cooled solution was irradiated with three 300 W incandescent bulbs arranged around the outside Pyrex test tube less than a cm from the exterior of the test tube wall. Within 3 h of irradiation, some crystal formation was noted on the wall of the interior test tube. After irradiating for 24 h, crystals had formed on the wall of the interior test tube and the solution remained deep red in color. The crystals were isolated via vacuum filtration to afford 15.5 mg (65% yield) of **6**.

### 5.3. Computational Details

Ground state geometry optimization of MeTAD was carried out at the B3LYP/6-311+G(d,p) level of theory, while the excited state electronic calculations were carried out using the TDDFT method as implemented in the Gaussian 16 (Revision B.01) suite of software [19], according to the identical computational protocol laid out by Chattaraj for vertical electronic excitations [14]. A frequency calculation on the ground state geometry was conducted at the same level of theory to ensure that the geometry represented a true minimum (i.e., no imaginary frequencies). The Multiwfn software package (version 3.8) was employed for calculation of the electrophilicity indices [20].

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/org4020013/s1>: For novel compound 6: <sup>1</sup>H NMR spectrum, <sup>13</sup>C NMR spectrum, IR spectrum, HRMS spectra. For known compounds 5 and 7: <sup>1</sup>H and <sup>13</sup>C NMR spectra. Output files from computational work.

**Funding:** This research was funded by Berry College.

**Data Availability Statement:** Copies of spectral data for novel compound 6, and known compounds 5 and 7, and output files from computational work are available in the Supplementary Materials.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. De Bruycker, K.; Billiet, S.; Houck, H.A.; Chattopadhyay, S.; Winne, J.M. Triazolinediones as Highly Enabling Synthetic Tools. *Chem. Rev.* **2016**, *116*, 3919–3974. [CrossRef]
2. Wamhoff, H.; Wald, K. Zur Photolyse und Thermolyse von 4-Aryl-1,2,4-triazolin-3,5-dionen. *Chem. Ber.* **1977**, *110*, 1699–1715. [CrossRef]
3. Amey, R.L.; Smart, B.E. Bicyclo[1.1.0]butanes. Reactions with Cyclic Azo Compounds. *J. Org. Chem.* **1981**, *46*, 4090–4092. [CrossRef]
4. Breton, G.W.; Hoke, K.R. Application of Radical Cation Spin Density Maps toward the Prediction of Photochemical Reactivity between N-Methyl-1,2,4-triazoline-3,5-dione and Substituted Benzenes. *J. Org. Chem.* **2013**, *78*, 4697–4707. [CrossRef] [PubMed]
5. Kjell, D.P.; Sheridan, R.S. Photochemical Cycloaddition of N-Methyltriazolinedione to Naphthalene. *J. Am. Chem. Soc.* **1984**, *106*, 5368–5370. [CrossRef]
6. Kjell, P.; Sheridan, R.S. A Photochemical Diels-Alder Reaction of N-Methyltriazolinedione. *J. Photochem.* **1985**, *28*, 205–213. [CrossRef]
7. Hamrock, S.J.; Sheridan, R.S. Photochemical Diels-Alder Addition of N-Methyltriazolinedione to Phenanthrene. *Tetrahedron Lett.* **1988**, *29*, 5509–5512. [CrossRef]
8. Hamrock, S.J.; Sheridan, R.S. Para Photoaddition of N-Methyltriazolinedione to Benzene. Synthesis of Energy-Rich Azo Compounds Comprising Benzene + N<sub>2</sub>. *J. Am. Chem. Soc.* **1989**, *111*, 9247–9249. [CrossRef]
9. Breton, G.W.; Newton, K.A. Further Studies of the Thermal and Photochemical Diels-Alder Reactions of N-Methyl-1,2,4-triazoline-3,5-dione (MeTAD) with Naphthalene and Some Substituted Naphthalenes. *J. Org. Chem.* **2000**, *65*, 2863–2869. [CrossRef] [PubMed]
10. Himbert, G.; Henn, L. Intramolecular Diels-Alder Reaction of Allencarboxanilides. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 620. [CrossRef]
11. Southgate, E.H.; Pospech, J.; Fu, J.; Holycross, D.R.; Sarlah, D. Dearomative Dihydroxylation with Arenophiles. *Nat. Chem.* **2016**, *8*, 922. [CrossRef] [PubMed]
12. Okumura, M.; Sarlah, D. Arenophile-Mediated Dearomative Functionalization Strategies. *Synlett* **2018**, *29*, 845–855.
13. Risi, F.; Pizzala, L.; Carles, M.; Verlaque, P.; Aycard, J.-P. Photolysis of Matrix-Isolated 4-R-1,2,4-triazoline-3,5-diones: Identification of Aziridine-2,3-dione Transients. *J. Org. Chem.* **1996**, *61*, 666–670. [CrossRef] [PubMed]
14. Patra, S.G.; Mondal, H.; Chattaraj, P.K. Variation in Electrophilicity on Electronic Excitation. *J. Phys. Org. Chem.* **2022**, e4359. [CrossRef]
15. Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, NY, USA, 1998; p. 30.
16. Breton, G.W.; Turlington, M. Alternative Synthetic Routes to N-Methyl-1,2,4-Triazoline-3,5-Dione (MeTAD) and Other Triazoline-dione Derivatives. *Tetrahedron Lett.* **2014**, *55*, 4661–4663. [CrossRef]

17. Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Van Speybroeck, V.; Winne, J.M.; Du Prez, F.E. Triazolinediones Enable Ultrafast and Reversible Click Chemistry for the Design of Dynamic Polymer Systems. *Nat. Chem.* **2014**, *6*, 815–821. [[CrossRef](#)] [[PubMed](#)]
18. Bausch, M.J.; David, B.; Dobrowolski, P.; Guadalupe-Fasano, C.; Gostowski, R.; Selmarten, D.; Prasad, V.; Vaughn, A.; Wang, L.-H. Proton-Transfer Chemistry of Urazoles and Related Imides, Amides, and Diacyl Hydrazides. *J. Org. Chem.* **1991**, *56*, 5643–5651. [[CrossRef](#)]
19. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 16, Revision B.01*; Gaussian, Inc.: Wallingford, CT, USA, 2016.
20. Lu, T.; Chen, F.J. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592. [[CrossRef](#)] [[PubMed](#)]

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