# 1-Thia-3,4-diazolidine-2,5-dione Functionality: A Photochemical Synthon for the Azo Group

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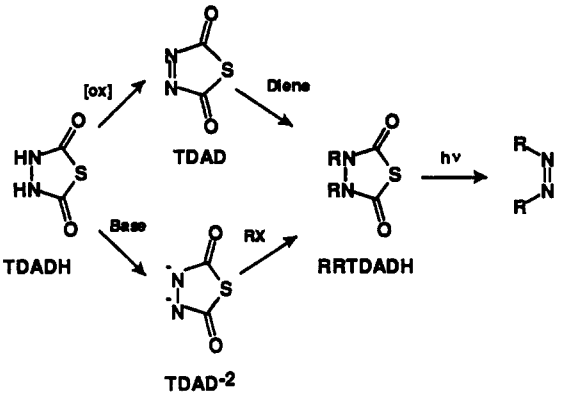
The 1-thia-3,4-diazolidine-2,5-dione functional group was shown to yield azo compounds upon photolysis. This photoreaction when combined with the known ability of this group to react in a Diels–Alder fashion or as a dinucelophile toward alkylating agents greatly increases the utility of this functionality. The dual reactivity of this group was demonstrated in the synthesis of a number of 3,4-dialkyl-1-thia-3,4-diazolidine-2,5-diones. The photolysis of these compounds produced either thermally stable cyclic azo compounds or the decomposition products of thermally unstable azo compounds.

While initially of historical importance as the main chromophoric functionality in organic dyes,[1] the azo moiety has been extensively used in synthesis; commonly being decomposed to form new carbon bonds.[2] More recently the facile thermal or photochemical decomposition of azo compounds has allowed their use in the production of a variety of diradicals,[3,4] strained ring compounds,[2–4] and other reactive or high-energy intermediates.[4,5] Unfortunately a major limitation on the use of this functionality has been exactly this facile decomposition, which limits the number of azo compounds which can be isolated.

There have been many routes developed for the synthesis of molecules containing the azo functionality.[2,6] However, the most ubiquitous synthetic method has been the addition of a nitrogen-containing dienophile, usually *N*-alkyl- or *N*-arylurazoles or N,N′-diester azo compounds,[2,5] in a Diels–Alder or 2 + 2 addition method to dienes and alkenes. The subsequent products are hydrolyzed to the corresponding hydrazines which are oxidized to the azo compounds. Unfortunately both the hydrolysis and oxidation steps often require quite harsh conditions[7] which can destroy many unstable hydrazines or azo compounds.

There have been many attempts to develop a pathway to azo compounds which avoid these harsh conditions. The most notable of these involve the synthesis of nitrogen-containing dienophiles such as 1,2-bis(β-tosylethoxycarbonyl)diazene[5] and 1,2-bis(β,β,β-trichloroethoxycarbonyl)-diazene,[8] which are designed to be much more easily hydrolyzed than the urazoles resulting from the use of the more common dienophiles. Other attempts have involved developing mild hydrolysis conditions for the more common dienophiles,[9] and a variety of methods have been used for the oxidation step which can sometimes be carried out at moderately low temperatures.[5,10]

**Scheme I**




In two little-noticed articles, the 3,4-dialkyl-1-thia-3,4-diazolidine-2,5-dione (RRTDADH) moiety was presented as a precursor to the azo functionality which was easily hydrolyzable.[11,12] This system is easily synthesized[13] and the oxidized form, 1-thia-3,4-diazoline-2,5-dione (TDAD), shows nearly the same Diels–Alder reactivity as the related *N*-alkyltriazoline-2,5-diones, though it is less stable and decomposes at low temperatures.[12] In addition, in a manner reminiscent of hydrazine dialkylation, it is readily deprotonated and the dipotassium salt can act as a dinucleophile with alkyl halides to produce a variety of other RRTDADHs[12] (Scheme 1).

We felt the RRTDADHs had the further potential advantage of photochemically cleaving directly to azo compounds and two small stable molecules (CO and COS)

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(9) Adam, W.; Arias, L. A.; De Lucchi, O. *Synthesis* **1981**, 543.
(10) (a) Crawford, R. J.; Mishra, A.; Dummel, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3959. (b) Kjell, D. P.; Sheridan, R. S. *J. Am. Chem. Soc.*, **1986**, *108*, 4111–4114.
(11) Corey, E. J.; Snider, B. B. *J. Org. Chem.* **1973**, *38*, 3632–3633.
(12) Beak , P.; Moje, S. W. *J. Org. Chem.* **1974**, *39*, 2951–2956.
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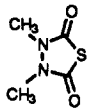
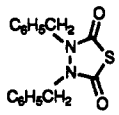
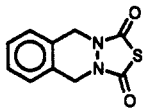
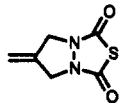
**Table 1. Yields of 3,4-Dialkyl-1-thia-3,4-diazolidine-2,5-diones via Alkylation of TDADH, and Photolysis Yields to Azo Compound**

| RRTDADH | yield, %[a] | azo compd[b] yield, % (conv, %) |
|---|---|---|
|  1 | 78 | *Z*, 44 (86)<br>*E*, 42<br>hydrazine, 14 |
|  2 | 19 | *Z*, 11 (33)<br>*E*, 32<br>hydrazine, 57 |
|  3 | 67[c] | 57 (40) |
|  4 | 30[d] | 97 (83) |

[a] Isolated yields. See Experimental Section for alkylation method. [b] Yields are NMR yields based on the amount of RRTDADH consumed in the photolysis reaction. The number in parentheses is the percent conversion of the RRTDADH starting material. [c] 100% NMR yield. [d] 85% NMR yield.

unlike the *N*-alkyltriazolines and other azo precursors which are not readily photochemically labile.[6c] Indeed we have found that the RRTDADHs are convenient photochemical azo precursors. Irradiation at 254 nm photochemically cleaves the TDADH ring but the resulting azo compound often absorbs little at these wavelengths.[4,14] Thus the azo compounds can be isolated, or can be decomposed either thermally or photochemically. The "dual" reactivity of TDADH and the subsequent photochemical cleavage of RRTDADHs makes this pathway to azo compounds a highly versatile and valuable route (Scheme 1). We have chosen to demonstrate the efficacy of this approach by synthesizing some well-characterized azo compounds photochemically. A variety of other azo compounds which are thermally unstable have also been produced, although not directly observed.

## Results and Discussion

**Dialkylation of TDADH.** TDADH has received "bad press" based mainly on the thermal instability of the oxidized form.[2] However, it has not been appreciated that dialkylation of TDADH to produce RRTDADHs greatly increases the usefulness of this functional group.[12] We have reinvestigated this reaction and found it to be quite versatile. As reported in Table 1 we have synthesized various RRTDADHs in good yields. For reasons detailed below we have repeated the synthesis of **1** and **2** made previously by Moje and Beak[12] who originally demonstrated the utility of this method by also synthesizing 3,4-diallyl- and 3,4-di-*tert*-butyl-TDADH.

The formation of the anion of this functional group proceeds quite readily. We measure a p$K_a$ of 3.5 while the *N*-methylurazole analog has a p$K_a$ of 5.7, a difference perhaps reflecting the greater aromaticity of a sulfur-containing ring compared to a nitrogen heterocycle, i.e. thiophene as compared to pyrrole.[15] The second p$K_a$ of the TDADH system could not be measured, but appears to be between 12 and 16 because the dianion can be formed with KOH.

Dialkylation can be accomplished in a variety of ways. The dianion has been isolated by adding 2 equiv of KOH to an aqueous solution of TDADH, removing the water, and drying the salt.[12] The dianion is slightly soluble in THF and quite soluble in DMF though we have found the best method for using it appears to be heating a mixture of 2 equiv of the alkylating agent, usually an alkyl halide, and the $TDAD^{-2}$ in THF with a small amount of DMF added.

Dialkylation can proceed through monoanions by simply stirring under a nitrogen atmosphere the alkylating agent and TDADH in refluxing acetonitrile along with 2 equiv of triethylamine. Perhaps even more convenient is to simply seal this solution in a tube and heat at 60 °C overnight. All of these methods give good yields and little attempt has been made to optimize those yields reported in Table 1.

Diacylation however was unsuccessful. The reaction of the dipotassium salt of TDADH with benzoyl chloride has been reported to produce an unidentified, moisture-sensitive solid.[12] When 2 equiv of benzoyl chloride is added to a solution of TDADH and 2 equiv of triethylamine in dry acetonitrile and the resulting solution is heated to reflux for 3 days, a white crystalline solid is isolated. The $^1H$ and $^{13}C$ NMR of this compound show two nonequivalent aromatic rings and three nonaromatic quaternary carbons. Neither the N–N diacylated product nor the possible O–N diacylated product fit this spectral data. A molecular ion of 266, the NMR spectra, and a negative $PbNO_3$ test for sulfur (all RRTDADHs gave a positive test for sulfur) suggest the known compound **7**[16] (Scheme 2).

When 2 equiv of benzoyl cyanide is added to a solution of TDADH and triethylamine in acetonitrile-$d_3$, $^1H$ NMR shows a major and a minor product produced in a 10:1 ratio after 4 h. The minor product completely converted to the major after 1 day at room temperature. When methylene chloride was used as the solvent, the former minor product was the only product and it was isolated as off-white crystals. We originally felt slow acylation might be occurring and that the "minor product" could be the mono-N-acylated TDAD-adduct **5**, which is an example of a class of compounds that has been previously observed.[17] That this was not the case was shown by the $^{13}C$ NMR of this compound which showed two nonaromatic quaternary carbons. A negative test for sulfur and mass spectral data indicating a MW = 162 g/mol showed that this is 5-phenyl-1,3,4-oxadiazolin-2(3*H*)-one (**6**)[16] with further acylation producing **7**.

Two equivalents of benzoyl chloride, cyanide, or anhydride all gave **7** as the major product in their reactions with TDADH and changing the base to the less nucleophilic diisopropylethylamine had no effect on the products formed. Thus Scheme 2 shows what we believe to be the

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**Scheme II**

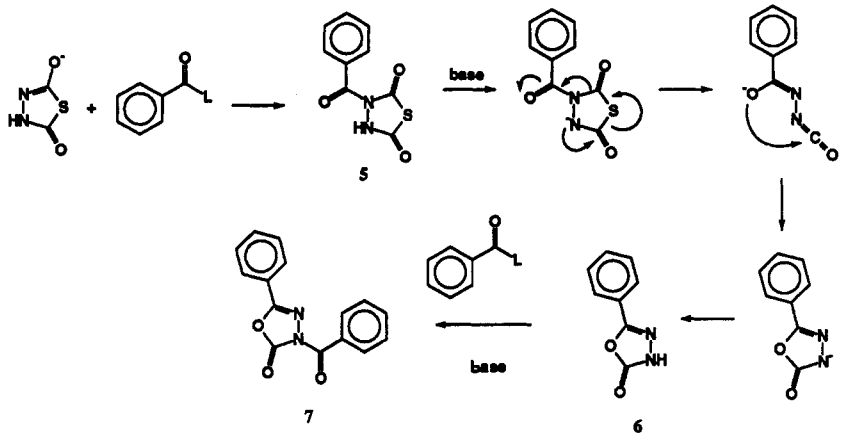
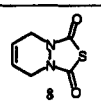
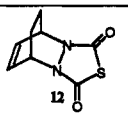
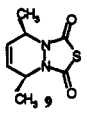
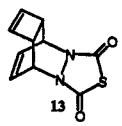
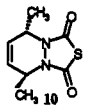
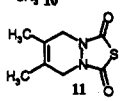
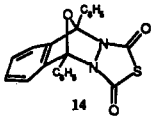



**Table 2. Yields of 3,4-Dialkyl-1-thia-3,4-diazolidine-2,5-diones from Diels–Alder Reaction and Yields of Photolysis to 1,3-Dienes**

| RRTDADH | Diels–Alder[a] yield, % | 1,3-diene[b] yield, % (conv, %) | RRTDADH | Diels–Alder[a] yield, % | 1,3-diene[b] yield, % (conv, %) |
|---|---|---|---|---|---|
|  8 | 75 | 61 (70) |  12 | 62 | CHD, 32 (22)<br>ZHT, 47<br>EHT, 21 |
|  9 | 67 | *E,E*, 100 (10) |  13 | 19 | BOT 100 (2), 86 (6)<br>COT 5<br>benzene 9 |
|  10 | 75 | *E,Z* 84 (7), 37 (84)<br>*Z,Z*, 6, 17<br>*Z,Z*, 10, 24 | | | |
|  11 | 50 | 85 (88) |  14 | 57 | |

[a] Isolated yields. See Experimental Section for method. [b] Yields are NMR yields of photolysis with 254 nm. The number in parentheses is the percent conversion of the RRTDADH starting material. See Experimental Section for details.

most reasonable route to **7** and **6**. Interestingly the 1,3,4-oxadiazol-2(3*H*)-one functionality of **7** and **6** is quite biologically active[18] and Scheme **2** may represent a facile route to this functionality.

**Diels–Alder Reaction of TDAD.** The dienophile character of TDAD has been established previously[11,12] and shown to be quite reactive. The dienophile can be formed from TDADH with several oxidizing reagents though we have used *tert*-butyl hypochlorite in most cases. Several RRTDADHs were synthesized in good yields by reaction of TDAD with the appropriate diene usually in acetone at low temperatures (Table 2). Compounds **8–12** have been synthesized previously[11,12] while the *N*-methyltriazoline-3,5-dione adduct similar to **13** has been reported.[6b]

**Nonconcerted Diels–Alder Reaction of TDAD.** *N*-Phenyl-1,2,4-triazoline-3,5-dione has been shown to react to form some Diels–Alder products via a step-wise mechanism.[19,20] When *N*-phenyl-1,2,4-triazoline-3,5-dione was reacted with (*Z,Z*)-2,4-hexadiene, which is sterically blocked from adopting a s-cis conformation, a diazetidene intermediate was seen by low-temperature NMR. This rearranged to a Diels–Alder adduct when warmed or, when in the presence of acidic methanol, was trapped to produce allylic methyl ethers.[20] TDAD has been shown to have nearly the same Diels–Alder reactivity as MTAD, and we were interested if it too adopted this stepwise mechanism of Diels–Alder addition.

When a solution of (*Z,Z*)-2,4-hexadiene in acetone-$d_6$ was added at −100 °C to a solution of TDAD in acetone-$d_6$ free of any remaining oxidant, $^1$H NMR (−95 °C) showed excess diene and three new sets of resonances a–c (see Experimental Section). After 2 h at −95 °C, $^1$H NMR showed complete decay of the set of "b" resonances and a concomitant increase in the set of "c" resonances. No further change was seen in the NMR spectra on warming the sample to room temperature.

Neither of the two final products formed was a Diels–Alder adduct, and to assign structures to these two products we compared chemical shifts and coupling constants to the trapped zwitterionic products reported by Foote.[20] Due to the thermal instability of TDAD, it must be generated immediately before diene addition and cannot be isolated and purified as can *N*-phenyl-1,2,4-triazoline-3,5-dione. While preliminary NMR spectra when acetone-$d_6$ is used as solvent can show that no *tert*-butyl hypochlorite oxidant remains, the *tert*-butyl alcohol

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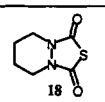
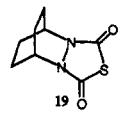
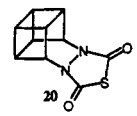
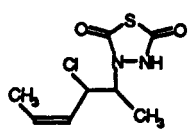
(19) Clennan, E. L.; Earlywine, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 7104.
(20) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376.

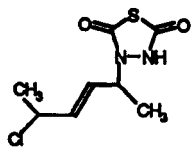
**Table 3. Yields of Saturated 3,4-Dialkyl-1-thia-3,4-diazolidine-2,5-diones and Yields of Photolysis to Azo Compounds**

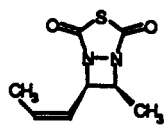
| RRTDADH | yield, %[a] | azo compd[b] hν yield, % |
|---|---|---|
|  18 | 58 | 90 |
|  19 | 74 | 100 |
|  20 | 51 | 80 |

[a] Isolated yield from unsaturated RRTDADH. See Experimental Section for method. [b] Isolated yield of photolysis. See Experimental Section for details.

and HCl which are generated cannot be removed. Thus, unlike the case with *N*-phenyl-1,2,4-triazoline-3,5-dione, trapping agents are always present and trapping can occur presumably by the HCl before rearrangement to Diels–Alder products. From a comparison of the observed chemical shifts and coupling constants to Foote's data we assign the structures **15** and **16** to the resonances a and c, respectively.


15

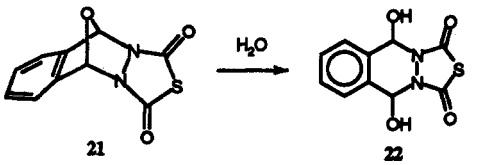

16


17

The identity of the transient species can also be assigned by comparison of chemical shifts and coupling constants to Foote's results, and we propose **17** which is analogous to the diazetidene seen by Foote.[20] The olefinic coupling of 9.77 Hz shows the double bond is in the cis configuration and coupling between the resonances at 4.85 and 4.13 ppm of 3.97 Hz suggests that it is the *cis*- rather than the *trans*-diazetidene. This intermediate is trapped exclusively as **15** as it slowly decomposes at −95 °C. The **16** present in the original spectrum may be from another diazetidene produced during the initial addition of diene when some warming might occur or from a competing route.

These results show that TDAD follows a similar path to *N*-phenyl-1,2,4-triazoline-3,5-dione when reacting with (*Z,Z*)-2,4-hexadiene. While there are several important differences in the reactions of TDAD with this and other dienes as compared to the concomitant reactions with *N*-phenyl-1,2,4-triazoline-3,5-dione which will be the subject of a subsequent paper, these preliminary results suggest that TDAD additions to dienes may be substantially more complicated than first believed.

**Modifications of 3,4-Dialkyl-1-thia-3,4-diazolidine-2,5-diones.** The RRTDADHs could be modified in a manner similar to the urazoles formed from *N*-alkyltriazolinediones and 1,3-dienes (Table 3). In particular the TDADH functional group is resistant to hydrogenation conditions[12] (**18** and **19**) and **13** could be photolyzed with triplet sensitization to the basketane-TDADH **20**. In addition activated zinc which was used to remove bromine from the precursor of **13** did not affect the TDADH functionality. An exception to this general stability of Diels–Alder TDAD/diene adducts was the adduct (**21**) of isobenzofuran and TDAD which hydrolyzed rapidly to diol **22**.



21 22

**Photochemistry of RRTDADH.** All RRTDADHs were photochemically reactive except for **14**, the adduct of diphenylisobenzofuran and TDAD. This lack of photoreactivity is likely due to a rapid radiationless decay route through the phenyl groups. Both broad-band quartz irradiation and 254-nm irradiation can be used to photolyze RRTDADHs which show a $UV_{max}$ at approximately 215 nm and a long tail to >285 nm. Irradiation at 254 nm is especially interesting because the azo functionality has an area of low absorbtivity (250–270 nm) between its $\pi-\pi^*$ and $n-\pi^*$ absorptions[4,21] where the TDADH group still has moderate absorption, and so the TDADH group can be photolyzed often without out affecting the resultant azo group. We were thus able to obtain in very high yields the azo compounds derived from our RRTDADHs when these species were thermally stable (Tables 1 and 3).

3,4-Dimethyl-1-thia-3,4-diazolidine-2,5-dione (**1**) and 3,4-dibenzyl-1-thia-3,4-diazolidine-2,5-dione (**2**) were originally isolated as oils and in this state were photochemically inactive, as was previously reported for the dibenzyl compound.[12] However, when prepared in a large batch, recrystallization or column chromatographic purification afforded colorless crystals for both compounds. This more highly purified form was found to be photochemically labile, so it may be that an O-alkylated impurity quenched the photochemistry of **1** and **2** and is responsible for the previously observed lack of photoreactivity and differences between our observed melting points and those reported earlier.[12] Initial formation of the cis isomer of both azomethane and 1,1′-diphenylazomethane was followed by photochemical isomerization to the trans isomer and isomerization to the hydrazone.[22] To the best of our knowledge, this is the first report of the observation of the cis isomer of 1,1′-diphenylazomethane. *cis*-Azomethane has been previously observed.[23] The photoisomerizations began to occur after less then 25% of **1** and 10% of **2** had been converted. No attempt was made to "fine tune" the wavelength of light in order to avoid this secondary photolysis.

Diazabasketene could be isolated after photolysis (254 nm) of the RRTDADH **20**. Upon photolysis (>285 nm) this azo compound produces 1,3,5,7-cyclooctatetraene (COT) and polymer; no cubane was observed.[24] Photolysis (>285 nm) in a glass (*tert*-butyl alcohol or 2-methyl-THF) of **20** was attempted, in the hope that COT was a product of an initially formed vibrationally "hot" cubane which would be more rapidly cooled in a solid rather than a solution. Disappointingly only COT was seen by $^1H$ NMR.

(21) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484.
(22) (a) O'Conner, R. *J. Org. Chem.* **1961**, *26*, 4375. (b) Blandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 5856.
(23) Ackermann, M. N.; Craig, N. C.; Isberg, R. R.; Lauter, R. M.; McPhail, R. A.; Young, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 1661.
(24) Snyder, J. P. Ph. D., Cornell University, 1966.

**β,γ-Unsaturated Cyclic Azo Compounds.** 1,4-Dihydrophthalazine, which has been previously observed,[25] was produced upon 254-nm irradiation of **3** at −90 °C. This compound is the most unstable azo compound yet isolated and is the only β,γ-unsaturated cyclic azo compound known. As has been noted previously[25] at higher temperatures (−45 °C) this azo compound decomposed to *o*-xylylene which then dimerizes. With the one exception of 1,4-dihydrophthalazine, when photolysis of a RRTDADH would lead to a β,γ-unsaturated cyclic azo compound only the diene which would be produced from the decomposition of the azo compound and its expected photoproducts were seen (Table 2).

The β,γ-unsaturated cyclic azo compounds associated with **11**−**13** could not be observed upon 254-nm, 260-nm (20-nm band-pass), or broad-band quartz irradiation even at −140 °C in dimethyl ether solution; again only dienes and diene photoproducts were observed. It is difficult to say if the resultant azo compounds are undergoing thermal or photochemical decomposition because the UV spectra of β,γ-unsaturated azo compounds are unknown. However, even with broad-band irradiation, observable amounts of product are seen from saturated RRTDADHs which produce thermally stable azo compounds, and of course 1,4-dihydrophthalazine could also be observed under these conditions. This suggests that unless there is a very large increase in the quantum yield for photodecomposition of β,γ-unsaturated cyclic azo compounds as compared to their saturated analogues, thermal decomposition of these molecules is occurring even at −140 °C. Further evidence suggesting thermal decomposition is that photolysis of **13** with very low conversion at low temperatures produces only bicyclo[4.2.0]octa-2,4,7-triene (BOT), the known thermal decomposition product of 7,8-diazatricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene, the azo compound which would be produced from **13**. The larger amount of energy involved in photochemical cleavage of this azo compound might be expected to produce COT as well as BOT. Thus the absence of COT may imply thermal decomposition. Rapid thermal decomposition of these β,γ-unsaturated cyclic azo compounds at −140 °C puts an upper limit of 10 kcal/mol for the loss of nitrogen from this group of azo compounds.

## Summary

We have demonstrated the utility of the 1-thia-3,4-diazolidine-2,5-dione functionality as a photochemical precursor for compounds containing an azo group. In addition the versatility of producing RRTDADHs by either Diels−Alder reaction or dialkylation adds to its significance. It is important to point out that TDAD, while less stable than the corresponding *N*-alkyltriazolinediones, has at least the same reactivity. However, if the use of TDAD is precluded by the need for high temperatures in a Diels−Alder reaction, an alternate route via dialkylation of $TDAD^{-2}$ by the 1,4-dihalo addition product of the requisite diene is readily available. This multifaceted synthetic approach to 3,4-dialkyl-1-thia-3,4-diazolidine-2,5-diones combined with their ability to photochemically produce the desired azo compound when irradiated with 254-nm light should make this route quite valuable and make hitherto unavailable azo compounds accessible.

## Experimental Section

**Materials.** Elution chromatography was carried out on Fisher 200−400 mesh type 60A silica gel. All commercially available reagents and solvents were purchased from Fisher or Aldrich chemical companies and used without further purification, unless otherwise noted. Dimethylformamide was distilled from Fisher 3-Å molecular sieves under reduced pressure immediately prior to use. Acetonitrile was distilled from calcium hydride under a nitrogen atmosphere immediately prior to use. Tetrahydrofuran was distilled from sodium under a nitrogen atmosphere immediately prior to use. 1,4-Dioxane was distilled from sodium under a nitrogen atmosphere immediately prior to use. A variety of deuterated solvents were employed for this work and used without further purification, including the following: acetone ($d_6$-99.8%D, C. I. L. and Aldrich), acetonitrile ($d_3$-100%D, Aldrich), chloroform ($d_1$-99.8%D, Aldrich), dimethyl sulfoxide ($d_6$-99.5%D, Stohler), methanol ($d_4$-99.5%D, Aldrich and Stohler/ICN), and tetrahydrofuran ($d_8$-99.8%D, Aldrich).

Dimethyl ether ($d_6$-99.5%D)[26] was prepared by sealing 8.0 mL of methanol-$d_4$ and 1.1 mL $d_2$-sulfuric acid in a Pyrex combustion tube and heating in a high pressure reactor to 250 °C (at 1200 psi) for 15 h. After cooling, the product mixture was frozen in liquid $N_2$, the combustion tube was opened and fitted with a no-air septum. The dimethyl ether-$d_6$ was distilled through two consecutive columns filled with KOH + 3-Å molecular sieves and $LiAlH_4$, respectively, giving ≈ 3 mL of pure, dry dimethyl ether-$d_6$. Commercial 5% sodium hypochlorite solution was used to prepare *tert*-butyl hypochlorite.[27]

**Irradiation Sources.** Three different ultraviolet light sources were employed for these experiments. Broad-band irradiations were carried out using an Oriel-6141 1000-W Hg(Xe) arc lamp. Irradiations at 254 nm were carried out in a homemade rayonet reactor comprised of twelve 25-W mercury vapor bulbs, General Electric no. G25T8. Irradiations at specific wavelengths, other than 254 nm, were carried out using a Photon Technology L1 Illumination system equipped with a 200-W Hg(Xe) arc lamp and monochrometer.

**Analytical Instrumentation.** NMR spectra were obtained using a Bruker AM-400 MHz spectrometer. Coupling constants are reported in hertz. Ultraviolet spectra were obtained on a Hewlett-Packard 8452A Diode Array Ultraviolet/visible spectrophotometer. Gas chromatograms were obtained using a Varian 5800 Capillary gas chromatograph with a 30-m DB5 J&W Scientific capillary column.

**Low-Temperature Photolysis Apparatus.** Attempts were made to produce thermally unstable cyclic azo compounds using an apparatus to perform low-temperature solution-phase photolyses which has been described previously.[28]

**p$K_a$ Measurements.** Potentiometric titrations of TDADH and MTAD were performed using standardized sodium hydroxide. The p$K_a$ was found from a plot of pH vs vol of NaOH.

**Preparations. 1-Thia-3,4-diazolidine-2,5-dione (TDADH).** TDADH was synthesized according to Rufenacht.[13] Care should be taken in the final step which involves hydrolytic production of TDADH with an aqueous solution of hydroiodic acid as the TDADH will sublime from the solution when the acid is removed under reduced pressure. $^{13}C$ NMR (DMSO-$d_6$) showed a single resonance at 163.8 ppm, mp 258 °C.

**Dipotassium Salt of TDADH.** TDADH (302 mg, 2.56 mmol) was dissolved in 51 mL of 0.10 M KOH. The water was removed under reduced pressure and the resulting colorless solid dried overnight in a vacuum desiccator. $^{13}C$ NMR (DMSO-$d_6$) showed one resonance at 167 ppm.

**Dialkylation. General Method 1.** The dipotassium salt of TDADH was suspended in dry DMF or a dry DMF/THF mixture, and 10 equiv of the appropriate alkyl halide was added. This solution was stirred under a nitrogen atmosphere and then transferred to a separatory funnel to which diethyl ether or methylene chloride was added. This mixture was washed with two portions of distilled water and one portion of a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude RRTDADH was crystallized or flash chromatographed through a silica column with diethyl ether

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as the eluant. In the latter case the ether was removed under reduced pressure and the resulting solid was recrystallized.

**Dialkylation. General Method 2.** An acetonitrile solution of 1 equiv of TDADH and 2 equiv each of alkyl halide and triethylamine was stirred under a nitrogen atmosphere at room temperature or at reflux. Alternately, the mixture was put in a sealed tube and degassed by bubbling with nitrogen. The tube was sealed and kept at the appropriate temperature. After reaction was complete, the solvent was removed under reduced pressure and water was added. This solution was extracted with ether which was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the crude 3,4-dialkyl-1-thia-3,4-diazolidine-2,5-dione was crystallized or flash chromatographed through a silica column with diethyl ether as the eluant. In the latter case the ether was removed under reduced pressure and the resulting solid was recrystallized.

**3,4-Dimethyl-1-thia-3,4-diazolidine-2,5-dione (1).** Method 1 was used with 2.56 mmol of the dipotassium salt and 25.6 mmol of iodomethane in 20 mL of dry DMF. After stirring 24 h at room temperature, 356 mg of an orange oil was obtained as crude product. After flash chromatography and recrystallization from pentane/methylene chloride, 296 mg (2.03 mmol, 78% yield) of large colorless needles mp 115–117 °C were obtained. The $^1$H NMR spectrum ($CDCl_3$) consisted of a single peak at 3.31 ppm. Mass spectrum (70 eV) *m/e* (rel inten) 146.0 (72.8), 86.1 (21.6), 58.1 (43.3), 43.0 (100.0). Expected molecular weight is 146 g/mol.

**3,4-Dibenzyl-1-thia-3,4-diazolidine-2,5-dione (2).** Method 2 was used with 0.748 mmol of benzyl bromide, 0.740 mmol of triethylamine, and 0.370 mmol of TDADH. After stirring at room temperature under a nitrogen atmosphere for 2 days. The standard workup resulted in 79.5 mg of a clear colorless oil. This oil was flash chromatographed and recrystallized from ether/pentane giving 21 mg (0.071 mmol, 19% yield) of large colorless crystals (mp 112–113 °C). The $^1$H NMR spectrum ($CDCl_3$) consisted of resonances at 7.35 (m, 6H, 3.7, 9.4 Hz), 7.16 (m, 4H, 3.7, 9.4 Hz) and 4.81 (s, 4H) ppm. $^{13}$C NMR showed resonances at 49.7, 127.1, 128.7, 129.2, 133.8 and 164.0 ppm. Mass spectrum (70 eV) *m/e* (rel inten) 298.1 (34.7), 92.1 (37.1), 91.0 (100), 65.0 (26.6). Expected molecular weight is 298 g/mol. Synthesis via method 1 gave an identical product but with only a 11% overall yield.

**3-Thia-1,5-diaza-7,8-benzobicyclo[4.3.0]nona-2,4-dione (3).** Method 1 was used with 0.423 mmol of the dipotassium salt of TDADH and 0.381 mmol of α,α′-dibromo-*o*-xylene in 28 mL of a 1:8 dry THF:DMF mixture. After 4 days of refluxing under nitrogen, standard workup with diethyl ether gave a light brown, oily solid. This material was flash chromatographed resulting in 62.0 mg (0.282 mmol, 67% yield) of a colorless solid mp 151–152 °C. The $^1$H NMR spectrum ($CDCl_3$) showed an AB quartet at 7.28 (3H, 6.99, 10.16 Hz) and 7.35 (2H, 6.99, 10.16 Hz) ppm and a singlet at 4.95 (4H) ppm. Mass spectrum (70 eV) *m/e* (rel inten) 221.1 (13.8), 220.1 (91.4), 105.1 (11.2), 104.1 (100), 103.1 (16.9), 78.1 (19.8), 77.1 (14.9), 52.5 (14.5), 51.0 (24.0), 39.0 (11.6). Expected molecular weight is 221 g/mol. Using this method with a sealed tube with acetonitrile-$d_3$ as solvent showed 100% conversion to product as monitored by NMR.

**7-Methylene-3-thia-1,5-diazabicyclo[3.3.0]octane-2,4-dione (4).** Method 2 was used with 0.190 mmol of 3-chloro-2-(chloromethyl)-1-propene, 0.195 mmol of TDADH, and 0.390 mmol of triethylamine in 300 mL of dry acetonitrile. A crystal of sodium iodide was added and the solution was refluxed for 48 h. Standard workup using methylene chloride gave a yellow oil which was flash chromatographed giving 10 mg (0.059 mmol, 30% yield) of a colorless solid, mp 106.5–108.5 °C. The $^1$H NMR spectrum ($CDCl_3$) showed a triplet at 4.4 (4H, 2.6 Hz) ppm and a quintet at 5.28 (2H, 2.6 Hz) ppm. Mass spectrum (70 eV) *m/e* (rel inten) 170.0 (36.1), 110.1 (11.7), 82.1 (34.4), 54.1 (100.0), 53.1 (16.6). Expected molecular weight is 170 g/mol. Using this method with a sealed tube with acetonitrile-$d_3$ as solvent showed 85% conversion to product as monitored by NMR.

**3-Benzoyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (7).** A procedure identical to dialkylation method 2 was used with 0.491 mmol of benzoyl chloride, 0.220 mmol of TDADH, and 0.402 mmol of triethylamine in 20 mL of dry acetonitrile. After heating to reflux under a nitrogen atmosphere for 3 days, standard workup with methylene chloride gave 47.2 mg of a colorless oil which crystallized on standing. This was recrystallized from ether/pentane giving 15 mg (0.056 mmol, 25.6% yield) of off-white crystals mp 134–136 °C (lit.[16a] mp 136–137 °C). The $^1$H NMR spectrum ($CDCl_3$) showed resonances at 7.78 (dd, 2H, 2.7, 9.45 Hz), 7.73 (dd, 2H, 2.7, 9.4 Hz), 7.54 (dt, 1H, 1.62, 8.1 Hz), 7.44 (dt, 1H, 1.62, 8.1 Hz) and 7.36 (m, 4H, 1.62, 4.86, 8.1 Hz) ppm. Mass spectrum (70 eV) *m/e* (rel inten) 266.1 (3.5), 106.1 (8.9), 105.1 (100), 77.1 (37.9), 51.0 (11.3). Expected molecular weight is 266 g/mol.

**5-Phenyl-1,3,4-oxadiazol-2(3*H*)-one (6).** A procedure nearly identical to dialkylation method 2 was used with 0.596 mmol of benzoyl cyanide, 0.292 mmol of TDADH, and 0.584 mmol of triethylamine in 20 mL of methylene chloride. After stirring at room temperature under a nitrogen atmosphere for 5 days, the reaction mixture was flash chromatographed through a silica column with diethyl ether eluant. The diethyl ether was then removed under reduced pressure leaving 35.7 mg of an off-white solid. This was recrystallized from hexanes/methylene chloride giving 24.3 mg (0.150 mmol, 51.3% yield) of slightly off-white crystals mp 137–138 °C (lit.[16b] mp 138–139 °C). $^1$H NMR ($CDCl_3$) showed a very broad resonance at 9.5 ppm and additional resonances at 7.85 (2 H, dd, 5.05, 1.4 Hz) and 7.58–7.42 (3 H, m 5.4, 3.86, 4.1, 1.4, 6 Hz) ppm. $^{13}$C NMR showed resonances at 123.8, 125.8, 128.7, 154.7, and 155.4 ppm. Mass spectrum (70 eV) *m/e* (rel inten) 162.1 (100.0), 118.1 (64.6), 105.1 (21.7), 91.1 (20.4), 77.1 (54.9), 51.0 (28.4). Expected molecular weight is 162 g/mol.

**Solvent and Base Dependence of 1,3,4-Oxadiazol-2(3*H*)-one Formation.** Benzoyl cyanide (6.1 mg, $4.65 \times 10^{-2}$ mmol), was added to 600 μL of an acetonitrile-$d_3$ solution containing 2.8 mg ($2.37 \times 10^{-2}$ mmol) of TDADH and 6.7 μL of triethylamine ($4.74 \times 10^{-2}$ mmol) in a 5-mm NMR tube. After 4 h at room temperature, $^1$H NMR showed **6** and **7** in a 3:4 ratio with no remaining benzoyl cyanide.

Benzoyl cyanide (7.3 mg, $5.57 \times 10^{-2}$ mmol) was added to 600 μL of an acetonitrile-$d_3$ solution containing 2.9 mg ($2.46 \times 10^{-2}$ mmol) of TDADH and 8.7 μL ($4.52 \times 10^{-2}$ mmol) of diisopropylethylamine. After 4 days at room temperature, $^1$H NMR was identical to that obtained with triethyl amine as the base with both **6** and **7** present in roughly a 3:4 ratio.

Benzoyl cyanide (4.9 mg, $3.73 \times 10^{-2}$ mmol) was added to a 600-μL methylene chloride-$d_2$ solution containing 2.6 mg ($2.20 \times 10^{-2}$ mmol) of TDADH and 5.9 μL ($4.23 \times 10^{-2}$ mmol) of triethylamine in a 5-mm NMR tube. After 14 h at room temperature, $^1$H NMR showed only resonances corresponding to **6**.

**Diels–Alder Reactions with TDAD.** Beak's method[12,29] was used for the synthesis of compounds **8–14** except that *tert*-butyl hypochlorite was used to oxidize TDADH in every case.

**3-Thia-1,5-diazabicyclo[4.3.0]non-7-ene-2,4-dione (8).** An acetone solution of 250 mg (2.117 mmol) of TDADH was oxidized at −78 °C with 500 μL of *tert*-butyl hypochlorite, and 4.233 mmol of 1,3-butadiene was added to the resulting purple solution. The color disappeared over a period of 2 hours, and the solution was warmed to room temperature. The solvent was then removed under reduced pressure and the resulting colorless solid was recrystallized from pentane/methylene chloride to give 270 mg (1.588 mmol, 75% yield) of large needles, mp 121–122 °C. The $^1$H NMR ($CDCl_3$) showed two multiplets at 4.2 and 5.95 ppm.

**9–12** were prepared in a manner identical to that used for **8**, and yields are reported in Table 2. Care must be taken not to use a large excess of diene because the resulting decrease in the polarity of the solution decreases the stability of TDAD and results in lower yields. Spectra and melting points of **8–12** and **19** agree with those previously reported.[11,12,29]

**4-Thia-2,6-diaza-12,13-dibromotetracyclo[5.4.2.0$^{2,6}$.0$^{8,11}$]-tridec-9-ene-3,5-dione.** An acetone solution of TDAD was prepared by adding 418 μL of *tert*-butyl hypochlorite to 200.7 mg (1.7 mmol) of TDADH at −78 °C. 2,3-Dibromobicyclo[4.2.0]-octa-4,7-diene (2.29 g, 8.7 mmol), prepared by brominating 1,3,5,7-cyclooctatetraene, was added. The purple color of TDAD

(29) Moje, S. W. Ph.D., University of Illinois Urbana, 1974.

faded quickly and the solution was allowed to warm to room temperature. The acetone was removed under reduced pressure leaving a dark brown oil. This was treated with hot ethanol, and 4-thia-2,6-diaza-12,13-dibromotetracyclo[5.4.2.$0^{2,6}$.$0^{8,11}$]-tridec-9-ene-3,5-dione was triturated out as a white solid (325.6 mg, 0.584 mmol, 34% yield), which decomposes without melting at temperatures above 235 °C in a sealed tube. The $^1$H NMR ($CDCl_3$) showed resonances at 7.02 (m, 1H, 2.21, 5.88 Hz), 6.66 (m, 1H, 1.47, 4.78 Hz), 5.40 (m, 1H, 1.47, 4.78 Hz), 5.32 (m, 1H, 1.47, 4.41 Hz), 4.73 (m, 1H, 3.9, 6.6 Hz), 4.20 (dd, 1H, 2.6, 4.1 Hz) and 3.60 (m, 2H, 1.6, 2.6, 3.2 Hz) ppm, identical to the splitting patterns in the previously reported spectra of the corresponding *N*-phenyltriazoline-3,5-dione adducts.[6b]

**4-Thia-2,6-diazatetracyclo[5.4.2.$0^{2,6}$.$0^{8,11}$]trideca-9,12-diene-3,5-dione (13).** The dibromo adduct (187.5 mg, 0.625 mmol) was added as a solid to a dioxane solution containing a zinc/silver couple[30] and this was heated to reflux for 20 h under a nitrogen atmosphere. The solution was allowed to cool to room temperature and the zinc/silver couple was removed by vacuum filtration through Celite. The solvent was removed under reduced pressure to leave 75 mg (0.341 mmol, 54% yield) of a clear colorless oil which crystallized on standing, mp 105.5–106.8 °C. The $^1$H NMR ($d_3$-acetonitrile) showed multiplets at 6.28 (dd, 2H, 2.6, 4.04 Hz), 5.19 (quin, 2H, 3.31 Hz) and 3.23 (d, 2H, 3.0 Hz) ppm and a singlet at 6.02 (2H) ppm, identical to the splitting patterns in the previously reported spectra of the corresponding *N*-phenyltriazoline-3,5-dione adducts.[6b] The $^{13}$C NMR ($CDCl_3$) showed peaks at 161.5, 139.0, 126.9, 53.7 and 44.4 ppm. Mass spectrum (70 eV) *m/e* (rel inten) 220.1 (100.0), 159.1 (23.8), 131.1 (57.6), 118.1 (87.1), 117.1 (40.0), 101 (90.5), 103.1 (69.3), 91.1 (50.6), 90.1 (20.6), 81.1 (58.7), 78.1 (91.5), 77.1 (31.2), 53,1 (21.5), 52.0 (98.6), 51.0 (51.8), 50.5 (22.5), 39.0 (45.7). Expected molecular weight is 220 g/mol.

**4-Thia-2,6-diazahexacyclo[5.4.$0^{2,6}$.$0^{8,11}$.$0^{9,13}$.$0^{10,12}$]-tridecane-3,5-dione (20).** This 3,4-dialkyl-1-thia-3,4-diazolidine-2,5-dione was prepared by triplet-sensitized photolysis of **13** in acetone again in a manner similar to that used by Snyder with the corresponding *N*-methyltriazolinedione adduct.[6b] **13** (19.5 mg, 8.86 × $10^{-2}$ mmol) was dissolved in 3 mL of acetone in a Pyrex tube and capped with a no-air septum. Oxygen was removed by bubbling nitrogen gas through the sample for 30 min. The sample was then photolyzed with broad-band irradiation (>285 nm) for 2.5 h. The acetone was removed under reduced pressure leaving a yellow oil, which was flash chromatographed through a silica column with diethyl ether as eluant. The ether was removed under reduced pressure leaving 10 mg (4.54 × $10^{-2}$ mmol, 51.3% yield) of a colorless crystalline solid, mp 161.5–163 °C. The $^1$H NMR showed resonances at 5.74 (m, 2H, 2.12, 4.12, 6.6 Hz), 3.68 (m, 4H, 3.3, 6.6 Hz), and 3.24 (quin, 2H, 2.7 Hz) ppm and had identical splitting to the 1,2,4-triazoline-3,5-dione adduct.[6b] $^{13}$C NMR showed resonances at 37.5, 42.3, 46.8, and 158.6 ppm. Mass spectrum (70 eV) *m/e* (rel inten) 220.0 (98), 159.0 (22), 118.0 (91), 117.0 (33), 105.0 (27), 104.0 (100), 103.0 (95). Expected molecular weight is 220 g/mol.

**Diphenylisobenzofuran (DPIBF) TDAD-Adduct (14).** An acetone solution of 192 mg (1.63 mmol) of TDADH was oxidized at −78 °C with 387 μL of *tert*-butyl hypochlorite. A solution containing 439 mg (1.63 mmol) of 1,3-diphenylisobenzofuran in 3.5 mL of a 5/1 THF/acetone mixture was added to the resulting purple solution. The solution was allowed to stir at −78 °C, under a nitrogen atmosphere, for 5 h and then was warmed to room temperature. The solvent was removed under reduced pressure, and the resulting light yellow solid was recrystallized from hexane/methylene chloride to give 360 mg (0.932 mmol, 57% yield) of thick needles, mp 146.7–148.3 °C. The $^1$H NMR ($CDCl_3$) showed resonances at 7.02 (m, 2.8, 10.3 Hz), 7.29 (dt, 1.8, 7.5 Hz), 7.48 (dt, 1.8, 7.5 Hz), 7.83 (m, 2.8, 10.3 Hz), and 7.95 (dd, 1.5, 7.5 Hz) ppm. $^{13}$C NMR ($CDCl_3$) showed resonances at 166.5, 139.9, 137.1, 132.9, 130.3, 129.8, 129.6, and 128.3 ppm.

**6,10-Dihydroxy-3-thia-1,5-diaza-7,8-benzobicyclo[4.3.0]-nonane-2,4-dione (22).** An acetone solution containing 5 mg (0.042 mmol) of TDADH was oxidized at −78 °C with 9 μL of *tert*-butyl hypochlorite. An acetone solution containing 0.10 mmol of isobenzofuran (prepared by pyrolysis of 1,4-epoxy-1,2,3,4-tetrahydronaphthalene[31]) was rapidly cannulated into the deep purple TDAD solution at −78 °C and the color slowly faded over 1 h. The solution was warmed to room temperature and the solvent removed under reduced pressure leaving a clear colorless oil. This was crystallized from chloroform giving 8.1 mg (0.032 mmol, 76% yield) of a light yellow solid. $^1$H NMR ($CDCl_3$) showed resonances at 7.5 (4H, m), 6.5 (2H, d, 8 Hz), and 5.25 (2H, d, 8 Hz) ppm. The resonances at 6.5 and 5.25 ppm collapsed to a singlet and broad singlet, respectively, when $D_2O$ was added.

**3-Thia-1,5-diazabicyclo[4.3.0]nonane-2,4-dione (18).** A solution of **8** (48.2 mg, 0.283 mmol) in 10 mL of ethyl acetate was placed in a high-pressure bottle; 9.4 mg of 10% Pd/C was added, and the mixture was placed on a Parr shaker and was charged to 50 psi with hydrogen. After 24 h of hydrogenation, the Pd/C was removed by vacuum filtration through Celite, and the solvent was removed under reduced pressure leaving a clear colorless oil which crystallized on standing. This was recrystallized from pentane/methylene chloride giving 28 mg (0.163 mmol, 57.6% yield) of large colorless needles, mp 122–124 °C. The $^1$H NMR ($CDCl_3$) showed resonances at 1.85 (m, 3.10, 5.97 Hz) and 3.70 (m, 3.10, 5.97 Hz) ppm.

**4-Thia-2,6-diazatricyclo[5.2.2.0]undecane-3,5-dione (19).** A solution of **12** (4.5 mg, 0.736 mmol) in 15 mL of ethyl acetate was placed in a high-pressure bottle; 33 mg 10% Pd/C was added and the mixture was placed on the Parr shaker. The bottle was charged to 50 psi with hydrogen and allowed to react for 36 h. The Pd/C was removed by vacuum filtration through Celite, and the solvent was removed under reduced pressure leaving a clear colorless oil which crystallized on standing. This was recrystallized from pentane/methylene chloride giving 108 mg (0.545 mmol, 74.1% yield) of large colorless needles (mp 129–131 °C). The $^1$H NMR ($CD_3CN$) showed resonances at 4.56, 1.97, and 1.90 ppm, identical to the splitting patterns in the previously reported spectra of the corresponding *N*-phenyltriazoline-3,5-dione adduct.[6b]

**Diazetidine Intermediate in the Reaction of TDAD and (*Z*,*Z*)-2,4-Hexadiene.** A solution containing 0.017 M TDAD in 500 μL of acetone-$d_6$ was prepared by the oxidation of TDADH with *tert*-butyl hypochlorite at −78 °C in a 5-mm NMR tube. When $^1$H NMR (−95 °C) of this purple solution showed that the *tert*-butyl hypochlorite had been completely consumed, the sample was removed from the NMR and cooled to −100 °C and a solution containing 1.1 μL (9.64 × $10^{-3}$ mmol) of (*Z*,*Z*)-2,4-hexadiene dissolved in 50 μL of $d_6$-acetone was added at −100 °C. The sample was transferred to the NMR (−95 °C) and the $^1$H spectra showed unreacted diene at 5.47 and 1.66 ppm and three new sets of resonances: (a) 5.75 (m, 1.0, 5.19, 8.54, 15.14 Hz), 4.73 (m, 2.14, 6.41, 5.49, 8.54 Hz), 4.21 (q, 5.8 Hz), 1.48 (d, 5.8 Hz), and 1.08 (d, 6.41 Hz) corresponding to **15**; (b) 5.70 (m, 2.14, 9.77, 7.93 Hz), 4.85 (dd, 3.36, 8.85 Hz), 4.13 (dd, 3.97, 6.71 Hz), 1.72 (dd, 1.83, 7.02 Hz) and 1.42 (d, 6.71 Hz) corresponding to **17**; (c) 5.55 (m, 7.02, 10.99 Hz), 5.38 (m, 8.85, 10.99, 1.83 Hz), 4.45 (dd, 5.49, 8.85 Hz), 3.98 (dd, 6.1, 6.7 Hz), 1.62 (dd, 1.83, 7.02 Hz), and 1.37 (d, 6.71 Hz) ppm corresponding to **16**. Upon standing 2 h at −95 °C, $^1$H NMR showed complete decay of the resonances of **17** with a concomitant increase in the resonances of **16**. No further change was seen on warming the sample to room temperature.

**Photolysis of 3,4-Dialkyl-1-thia-3,4-diazolidine-2,5-diones. General Photolysis Method.** A 5-mm quartz NMR tube containing 600 μL of a solution of the 3,4-dialkyl-1-thia-3,4-diazolidine-2,5-dione in various solvents was capped with a no-air septum. The solution was deoxygenated by bubbling nitrogen gas through it for 10 m. The sample was irradiated at 254 nm for various times and the progress of the reaction was monitored by $^1$H NMR. Occasionally broad-band irradiation was used. In some instances the resulting azo compound was isolated by removing the solvent followed by column chromatography or recrystallization.

**Azomethane.** A 0.002 M solution of **1** in $d_3$-acetonitrile was degassed and irradiated with 254-nm light at room temperature for 5 min. $^1$H NMR showed the resonance of **1** had decreased,

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and a new resonance at 3.5 ppm, corresponding to *cis*-azomethane,[23] had appeared. Upon further photodecomposition of **1**, $^1$H NMR showed that the *cis*-azomethane underwent secondary photolysis and a new resonances at 3.65 ppm appeared, corresponding to the trans isomer[23] and at 6.35, 5.96 and 2.71 ppm corresponding to *N*-methylhydrazone. After 15 min of irradiation, 86% of **1** had been converted, yielding 12, 42 and 44% of the hydrazone and the trans and cis isomer of azomethane, respectively. An additional 5 min of irradiation completely converted **1** and gave 5, 60 and 16% yields of the hydrazone and the trans and cis isomer of azomethane, respectively.

**1,1'-Diphenylazomethane.** A 0.002 M solution of **2** in $d_3$-acetonitrile was degassed and irradiated with 254-nm light at room temperature for 30 s. $^1$H NMR showed the resonance of **1** had decreased, and a new singlet resonance at 4.65 ppm and multiplets at 7.47 and 7.55 ppm, presumably corresponding to *cis*-1,1'-diphenylazomethane, had appeared. Upon further photodecomposition of **2**, $^1$H NMR showed that the *cis*-1,1'-diphenylazomethane underwent secondary photolysis and the resonances of the trans isomer (s, 4.95; m, 7.49; m, 7.62 ppm)[22b] began to appear. Continued photolysis produced *N*-benzyl-1-phenylhydrazone (s, 2.90; s, 4.36; broad s, 6.4; m, 7.17; m, 7.30; m, 7.56 ppm). After 5 min of irradiation, 33% of **2** had been converted to a 1:3:2 mixture of the cis isomer, the trans isomer, and the hydrazone, respectively.

**1,4-Dihydrophthalazine.** A 0.008 M solution of **3** in THF-$d_8$ was degassed and irradiated with 254-nm light at −95 °C for 6 min. $^1$H NMR at −90 °C showed a mixture of the corresponding azo compound, 1,4-dihydrophthalazine,[25] and some photolytic byproducts. After 10 min of photolysis, $^1$H NMR showed that a steady-state concentration of 0.003 M in the azo compound had been established, while further irradiation increased the concentration of photo byproducts. When this solution was warmed to room temperature for 2 min and recooled to −90 °C, the $^1$H NMR spectrum showed complete decay of the azo compound and the production of *o*-xylene dimer.[25] Broad-band quartz irradiation at −108 °C and subsequent low-temperature NMR showed the same photochemistry but resulted in a lower steady-state concentration of the azo compound.

**4-Methylene-1,2-diazacyclopentene.** A 0.002 M solution of **4** in acetonitrile-$d_3$ was degassed and irradiated with 254-nm light at room temperature for 5 min. $^1$H NMR showed 83% conversion of **4** and a 97% yield of the known azo compound, 4-methylene-1,2-diazacyclopentene.[32]

**3,4,5,6-Tetrahydropyridazine.** A 0.002 M solution of **18** in acetonitrile-$d_3$ was degassed and irradiated with 254-nm light at room temperature for 20 min. $^1$H NMR showed complete conversion to 3,4,5,6-tetrahydropyridazine.[33] Further photolysis caused the known conversion of this azo compound to the hydrazone, 1,4,5,6-tetrahydropyridazine.[33] The azo compound could be isolated in 90% yield, but would isomerize to the hydrazone on standing at room temperature.[33]

**2,3-Diazabicyclo[2.2.2]-2-octene.** A 0.001 M solution of **19** in methanol-$d_4$ was degassed and irradiated with 254-nm light at room temperature for 15 min. 1H NMR showed complete conversion to 2,3-diazabicyclo[2.2.2]-2-octene.[34] The crystalline azo compound could be isolated in 100% yield, by removing the solvent under reduced pressure.

**Diazabasketene.** A 0.002 M solution of **20** in acetonitrile-$d_3$ was degassed and irradiated with 254-nm light at room temperature for 30 min. $^1$H NMR showed a 95% yield of diazabasketene[35] and 5% cyclooctatetraene. This azo compound could be isolated in 80% yield, by flash chromatography through a silica gel column with ether eluant.

A 0.002 M solution of **20** in *tert*-butyl alcohol was degassed, frozen, and irradiated with >285-nm light at 0 °C for 45 min. $^1$H NMR showed cyclooctatetraene and diazabasketene as the only products.

A 0.002 M solution of **20** in 2-methyl-THF was degassed, frozen, and irradiated with >285-nm light at −20 °C for 45 min. $^1$H NMR showed 1,3,5,7-cyclooctatetraene and diazabasketene as the only products.

**Photolysis of Unsaturated Analogs.** Photolysis of 0.01 M solutions in acetonitrile-$d_3$ of compounds **8**−**13** with 254-nm, broad-band quartz or >285-nm light at room temperature always gave the corresponding diene and diene photoproducts. The yields and percent product conversion are reported in Table 2. Photolysis of a 0.01 M solution of **9** in acetonitrile-$d_3$ at 260 nm, with a 20-nm band-pass, to 10% conversion by $^1$H NMR, produced exclusively the (*E*,*E*)-2,4-hexadiene (<0.1% (*E*,*Z*) isomer by GC analysis). Photolysis of **10** with 254-nm irradiation to 6.8% conversion produced 84, 5, and 11% (*E*,*Z*)-, (*Z*,*Z*)-, and (*E*,*E*)-2,4-hexadiene, respectively. At 84% conversion these ratios were 37:17:24.

**Low-Temperature Photolysis of 11−13. Photolysis of 11 in Methanol-$d_4$ at −90 °C.** A 0.001 M degassed methanol-$d_4$ solution of **11** in a 5-mm quartz NMR tube was cooled to −98 °C and irradiated with broad-band light for 15 s. The cold sample was transferred to the NMR spectrometer and a $^1$H spectra was obtained at −90 °C. This showed 9% conversion of **11** with only 2,3-dimethyl-1,3-butadiene (5.11 (bs, 1H), 5.02 (bs, 1H), and 1.93 (s, 3H) ppm) produced. The sample was warmed to room temperature for 10 min and recooled to −90 °C. $^1$H NMR showed no change.

**Photolysis of 12 at −140 °C in DME-$d_8$.** A 0.007 M degassed dimethyl ether-$d_6$ solution of **12** in a 5-mm quartz NMR tube was cooled to −140 °C and irradiated at 254 nm for 15 min after which the sample was frozen at −160 °C and transferred to the NMR. The sample was allowed to thaw in the probe at −135 °C and a $^1$H spectra obtained at −135 °C. This spectrum showed 22% conversion of **12**, and yields of 32, 47, and 21% were found for cyclohexadiene (CHD), (*Z*)-1,3,5-hexatriene (ZHT), and (*E*)-1,3,5-hexatriene (EHT), respectively. The sample was warmed in the probe to −40 °C for 10 min and recooled to −135 °C. No peaks which might correspond to the azo compound were observed. Photolysis of a 0.007 M degassed diethyl ether-$d_{10}$ solution of **12** in a 5-mm quartz NMR tube at −110 °C with broad-band quartz irradiation for 1 min resulted in a 20% conversion with yields of CHD, ZHT, and EHT of 49, 37, and 13%, respectively.

**Photolysis of 13 at 230 nm (12 nm band-pass) at −114 °C in Ether-$d_{10}$.** A 0.005 M degassed diethyl ether-$d_{10}$ solution of **13** in a 5-mm quartz NMR tube was cooled to −114 °C and irradiated at 230 nm (12-nm band pass) for 3 h. The cold sample was transferred to the NMR spectrometer and allowed to warm to −90 °C. $^1$H NMR (−90 °C) showed 2% conversion of **13**, and bicyclo[4.2.0]octa-2,4,7-triene (BOT) was the only additional species observed. The sample was removed from the NMR and while kept cold (−95 °C) redeoxygenated and photolyzed as above for an additional 5 h. $^1$H NMR (−90 °C) showed a 6% conversion of **13**, and 86, 5, and 9% respective yields of BOT, 1,3,5,7-cyclooctatetraene, and benzene, a BOT photoproduct. The sample was warmed to room temperature for 10 min and recooled. $^1$H NMR (−90 °C) showed a complete conversion of BOT to COT.

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