

A PHOTOCHEMICAL DIELS-ALDER REACTION OF *N*-METHYLTRIAZOLINEDIONE[†]

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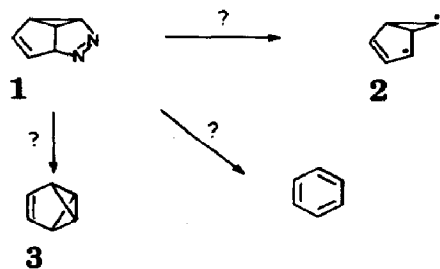
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Summary

Irradiation of *N*-methyltriazolinedione (MTAD) and naphthalene leads to a new [4 + 2] cycloadduct. Quantum yield data indicate that the reaction can occur via both singlet and triplet excited MTAD and also via charge transfer irradiation of a ground state complex. Naphthalene quenches the fluorescence of ¹MTAD at diffusion-controlled rates. A contact radical-ion pair is suggested as a common intermediate in the singlet and charge transfer reactions. Triplet sensitization of the cycloadduct caused di- π -methane rearrangement.

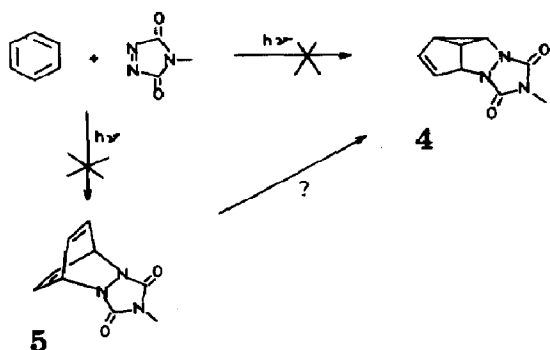
1. Introduction

In studies of reactive intermediates related to aromatic photochemistry we have sought diazasemibullvalene **1**. This fascinating unknown molecule is a potential precursor to the so-called prefulvene biradical **2**, suggested to be an intermediate in benzene and benzvalene photochemistry [1]. Alternatively, **1** might decompose directly to benzene and nitrogen in an extremely exothermic fashion or might give benzvalene **3** via a retro homo Diels-Alder reaction [2]:



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One potential precursor to 1 would be the corresponding urazole 4. This compound might, in turn, be generated by *meta* photoaddition of *N*-methyltriazolinedione (MTAD) to benzene. Alternatively, di- π -methane photorearrangement of a corresponding [2 + 4] adduct 5 of MTAD and benzene might give 4:



We have found, however, that under no conditions could a photoadduct between MTAD and benzene be observed. This is similar to reports by Wamhoff and Wald [3], although they found evidence for possible inefficient [2 + 2] addition. Askani and Schneider [4] have also reported unsuccessful attempts to generate azodicarboxylate-benzene adducts similar to 5, through more conventional synthetic routes.

In contrast with the above results, we have found that MTAD efficiently adds photochemically to naphthalene in a [4 + 2] fashion. Moreover, the reaction occurs on visible irradiation of MTAD, rather than on excitation of naphthalene. Triazolinediones exhibit a rich and varied thermal chemistry. Much of the interest in these compounds derives from their use as synthons for azo compounds [5]. Triazolinediones are extremely reactive dienophiles, and their [4 + 2] cycloadditions have been extensively studied [5, 6]. Reactions with reactive olefins can lead to electrophilic attack followed by rearrangement and ring closure [7]. A number of fascinating azo compounds have been generated in this fashion. Ene reactions and [2 + 2] cycloadditions are also observed between triazolinediones and appropriate olefins [7]. Finally, triazolinediones have been observed to add to strained σ bonds in bicyclobutanes and bicyclopentanes [8, 9].

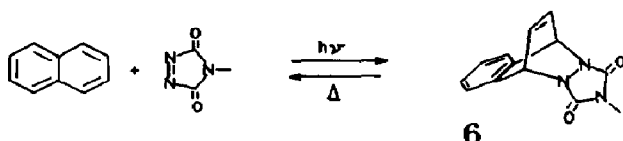
In contrast with the wide variety of thermal reactions of triazolinediones, their photoreactions have been little explored. Triazolinediones have been reported to undergo unimolecular decomposition [3] and polymerization on irradiation [10]. Excited triazolinediones also become good hydrogen atom abstractors and react readily with ethers [3]. Finally, light has been reported to accelerate the reaction of triazolinediones with reluctant bicyclobutanes [9]. Because of the paucity of information on the excited state behavior of triazolinediones we have taken some pains to explore the novel photoaddition of MTAD with naphthalene fully. These results are reported herein.

2. Experimental details

Preparative visible irradiations were performed in nitrogen-deaerated solutions using a 1000 W incandescent lamp. The solutions were maintained at about 18 °C with a cold-water jacket. Sensitized preparative irradiations were accomplished with a Rayonet photochemical reactor with 300 nm bulbs. Quantum yields were obtained with a Spectra Physics 164 argon ion laser operating at either 513.9 or 457.9 nm. The laser power was measured with a Scientech laser power meter; the absolute power through samples was calibrated with Reinecke's salt actinometry [11]. The product formation was assayed by visible spectroscopy, following disappearance of the MTAD absorption at 547 nm. The equality of MTAD disappearance and product formation was carefully ascertained by ^1H nuclear magnetic resonance (NMR) spectroscopy with an internal standard at several naphthalene concentrations. Control experiments showed the MTAD disappearance quantum yield to be less than 0.05 in the absence of naphthalene, in CCl_4 or CH_3CN . All quantum yield solutions were degassed with nitrogen. More rigorous freeze-thaw degassing had no effect. Full experimental details will be published elsewhere.

3. Results

Visible irradiation of MTAD and naphthalene leads to a new product. This compound can be purified by flash chromatography on silica gel and careful recrystallization from ethanol. The product, however, is thermally quite labile and regenerates starting materials readily above 40 °C. ^1H and ^{13}C NMR spectra indicate a highly symmetric 1:1 adduct, consistent with only the [4 + 2] adduct **6**:



The spectral properties of **6** have been published elsewhere [12].

The quantum yields of the photoaddition were obtained under various conditions. Direct absorption of MTAD at 514 nm produces photoproduct **6**. The quantum yields show an unusual dependence on the concentration of naphthalene, shown in Fig. 1. However, no dependence of the quantum yield on [MTAD] was observed. The quantum yields show a strong solvent polarity dependence. The limiting quantum yield in CCl_4 is 0.09, whereas that in CH_3CN is 0.03.

The reaction could also be triplet sensitized. Although the triplet energy of MTAD is not known, this value has been estimated to be about 40 kcal mol $^{-1}$ [13]. Thus, biacetyl ($E_T = 56.3$ kcal mol $^{-1}$) [14] should only transfer energy to MTAD, and not to naphthalene ($E_T = 60.9$ kcal mol $^{-1}$)

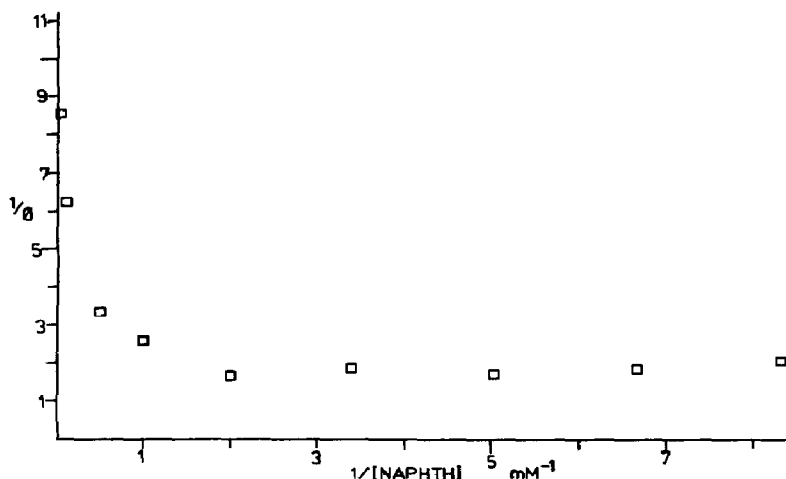


Fig. 1. Naphthalene concentration dependence of quantum yields for **6** formation ($[\text{MTAD}] = 0.6 \text{ mM}$; in CCl_4).

[14]. Irradiation of a solution of biacetyl (50 mM), naphthalene (1 mM) and MTAD (0.6 mM) in CCl_4 at 458 nm, where only biacetyl absorbs under these conditions, gave an addition quantum yield of 0.63.

At higher concentrations, naphthalene forms a charge transfer (CT) complex with MTAD. With difference spectroscopy the CT absorption at about 400 nm can be isolated, and is shown in Fig. 2. Treating the concentration dependence of CT absorption by a modified Benesi-Hildebrand method [15] gives a small complexation constant of 0.4 M^{-1} . Irradiation of only the CT complex at 458 nm also produces **6** with $\Phi_{\text{add}} = 0.09$ ($[\text{naphthalene}] = 500 \text{ mM}$; $[\text{MTAD}] = 0.6 \text{ mM}$).

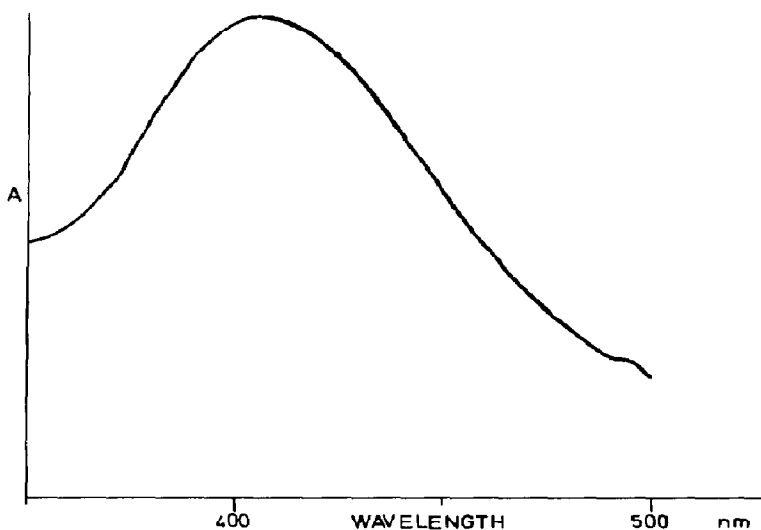


Fig. 2. CT absorption of the MTAD-naphthalene complex obtained by difference spectroscopy ($[\text{MTAD}] = 0.6 \text{ mM}$; $[\text{naphthalene}] = 1 \text{ M}$; in CCl_4).

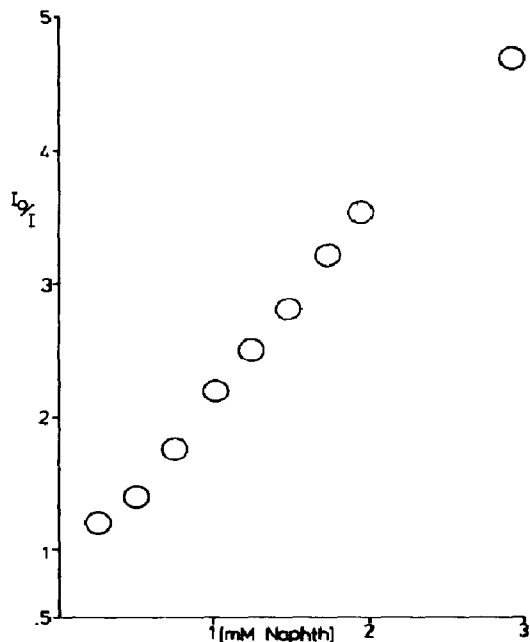


Fig. 3. Stern-Volmer plot for quenching of MTAD fluorescence in CCl_4 by naphthalene.

Naphthalene efficiently quenches the fluorescence of MTAD. A Stern-Volmer plot for the quenching is shown in Fig. 3. The slope gives a $k_q\tau$ value of 1540 M^{-1} . Use of an MTAD singlet lifetime of 77 ns (this value is somewhat larger than the 43 ns previously reported [13], although we have found that the singlet lifetime is quite sensitive to adventitious quenching) gives a quenching rate constant of $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This value is approximately equal to the diffusional rate constant in CCl_4 , reported to be $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [14].

4. Discussion

Although the photoreaction of MTAD with naphthalene to give 6 appears to be simple, the mechanism is surprisingly complex. The quantum yield data indicate that the reaction can proceed via both excited singlet and triplet MTAD. The high thermal reactivity of MTAD, and long singlet lifetime, render conventional triplet quenching studies difficult. The observation of diffusion-controlled quenching of $^1\text{MTAD}^*$ by naphthalene, however, provides a useful probe of both singlet and triplet reactivity. Comparison of quantum yields with the Stern-Volmer $k_q\tau$ value indicates that photoaddition at low naphthalene concentrations must involve triplet MTAD and at high naphthalene concentrations must involve singlet MTAD. These arguments have been presented in detail elsewhere [12].

A curved double-reciprocal plot, such as that shown in Fig. 1, was predicted by Dalton and Snyder [16] for photoadditions proceeding through both singlet and triplet states (and a similar interpretation was given by Das *et al.* [17]). Using steady state kinetics, these researchers derived

$$\frac{1}{\Phi} = \frac{({}^1k_q{}^1\tau + 1/[B])({}^3k_q{}^3\tau + 1/[B])}{\alpha{}^1k_q{}^1\tau({}^3k_q{}^3\tau + 1/[B]) + \beta\Phi_{ST}{}^3k_q{}^3\tau(1/[B])} \quad (1)$$

to describe the concentration dependence of the addition quantum yields. In eqn. (1), ${}^n k_q$ is the quenching rate constant for state n , ${}^n \tau$ is the inherent lifetime of state n , B is the trapping reagent, α is the fraction of quenched singlet that gives product, β is the fraction of quenched triplet that gives product and Φ_{ST} is the intersystem crossing efficiency. Unfortunately, β , Φ_{ST} and ${}^3 k_q{}^3 \tau$ are not known for MTAD and naphthalene. However, the fluorescence quantum yield for ${}^1\text{MTAD}^*$ is 5%, and Pocius and Yardley [13] have suggested that the rest of singlet decay is due to intersystem crossing. It is also clear from the high addition quantum yields at low naphthalene concentrations that triplet addition is quite efficient. It is interesting that the double-reciprocal plot in Fig. 1 is reproduced quite well by using ${}^1 k_q{}^1 \tau = 1540 \text{ M}^{-1}$ and $\alpha = 0.11$ (from the Stern-Volmer plot and Fig. 1 extrapolated to infinite naphthalene concentration) and on the assumption that $\Phi_{ST}\beta = 0.9$ and ${}^3 k_q{}^3 \tau = 15\,000 \text{ M}^{-1}$. For example, at [naphthalene] = 1 mM, $\Phi_{\text{calc}} = 0.30$ and $\Phi_{\text{meas}} = 0.30$ and, at [naphthalene] = 0.12 mM, $\Phi_{\text{calc}} = 0.51$ and $\Phi_{\text{meas}} = 0.49$. It must be stressed that these results are not conclusive, and the assumed values above have not been experimentally substantiated. These results do lend support, however, to the contention that both singlet and triplet MTAD react. If the interaction of ${}^3\text{MTAD}$ and naphthalene is diffusion controlled, the lifetime of ${}^3\text{MTAD}$ would be $1.5 \times 10^{-6} \text{ s}$. Pocius and Yardley [13] estimated that ${}^3\tau$ could not be greater than about $1 \times 10^{-6} \text{ s}$ on the basis of the lack of phosphorescence.

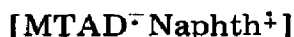
Only a few CT complexes of triazolinediones have been previously observed. *N*-phenyltriazolinedione has recently been reported to form observable CT complexes with 1,3-dimethoxybenzene ($\lambda_{\text{max}} = 456 \text{ nm}$) [18], 1,4-dimethoxybenzene ($\lambda_{\text{max}} = 457 \text{ nm}$) [18] and hexamethylbenzene ($\lambda_{\text{max}} = 448 \text{ nm}$) [19]. The CT absorption of the naphthalene-MTAD complex has the expected energy. Comparison of the reported CT absorption energies of the *N*-phenyltriazolinedione and tetracyanoethylene (TCNE) complexes with hexamethylbenzene [19] gives a difference of electron affinities of 0.9 eV. The assumption of a similar difference between the TCNE [20] and MTAD complexes with naphthalene predicts a λ_{max} of 396 nm for the MTAD complex. A second maximum, predicted to lie at 327 nm, would be obscured by the absorptions of free MTAD and naphthalene.

It is intriguing that direct CT irradiation of the MTAD-naphthalene complex and of singlet MTAD reaction extrapolated to infinite naphthalene concentration gives the same quantum yield. These results suggest the possibility of a common intermediate. The diffusion-controlled quenching of ${}^1\text{MTAD}^*$ by naphthalene is consistent with exothermic electron transfer.

Application of the Weller equation [21]

$$\Delta G = -E_S - E_D^{\text{ox}} + E_A^{\text{red}} + 0.32 \text{ eV} \quad (2)$$

with use of the solvation factor 0.32 suggested by Lewis [22] for non-polar solvents indicates that electron transfer from naphthalene to $^1\text{MTAD}^*$ should be exothermic by about 2 kcal mol^{-1} [12]. In contrast, irradiation of the CT absorption in the ground state complex should also give an electron transferred pair. We thus tentatively suggest that a common polar excited state complex or contact radical-ion pair **7** is involved:

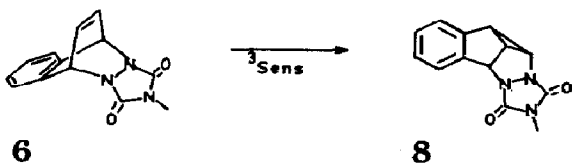


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Exciplexes common to both direct irradiation and CT complex excitation have been postulated before [21, 23, 24]. Unfortunately, we have not been able to observe luminescence from an exciplex in this system in either polar or non-polar solvents. We have found solvent effects consistent with the intermediacy of **7**, however. The limiting quantum yield for product formation drops by a factor of 3 to 0.03 in CH_3CN , compared with that in CCl_4 . This result is similar to observations in other reported photoreactions involving polar exciplexes [22, 23]. One possible explanation for this effect is that polar solvents induce separation of contact ion pairs to the extent that bond formation is no longer possible, but back electron transfer can give starting materials [22]. Interestingly, we see only a very small effect of solvent polarity on the primarily triplet quantum yields at low naphthalene concentrations.

Photochemically accelerated Diels-Alder reactions have been observed many times [20, 23, 25]. Although at first sight these reactions violate orbital symmetry principles, several researchers have pointed out that highly polar situations may ease these restrictions [25 - 27]. We have as yet no information on the concertedness of our cycloadditions. It is possible that the singlet exciplex forms an efficient funnel to the ground state surface at a point near the transition state for thermal Diels-Alder reaction. It is interesting that Fukuzumi and Kochi [20] have found that the activation energies for TCNE aromatic Diels-Alder reactions closely approximate the predicted energetics for electron transfer. In our case, however, the reaction is endothermic and only occurs on electronic excitation.

We have found that **6** serves as a potential precursor to the benzo analog of our target molecule **1**. Triplet-sensitized irradiation (xanthone at 300 nm) of **6** clearly gives **8** via di- π -methane rearrangement:



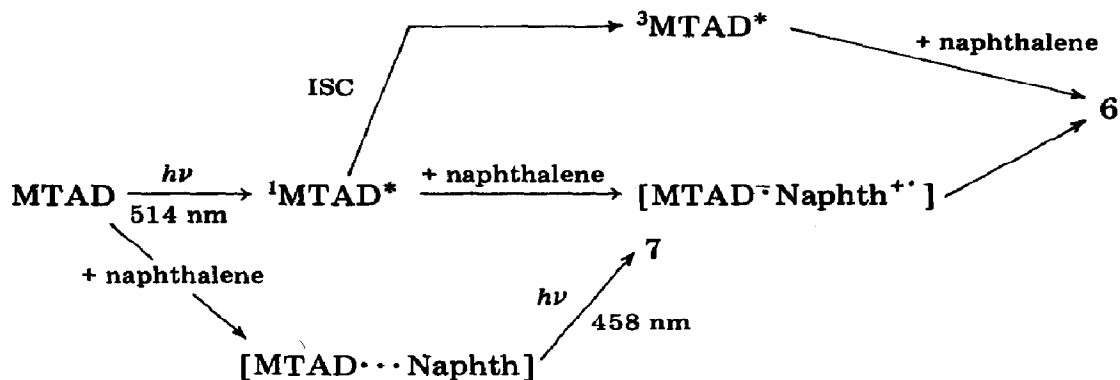
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We are currently attempting the conversion of **8** to the corresponding azo compound.

5. Conclusions

We have shown that irradiation of MTAD and naphthalene gives the [4 + 2] cycloadduct **6**. Quantum yield data suggest that the reaction can proceed via both singlet and triplet MTAD and also by direct CT excitation. The results are consistent with the tentative scheme shown below:



Acknowledgments

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