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Unexpected σ Bond Rupture during the Reaction of *N*-Methyl-1,2,4-triazoline-3,5-dione with Acenaphthylene and Indene

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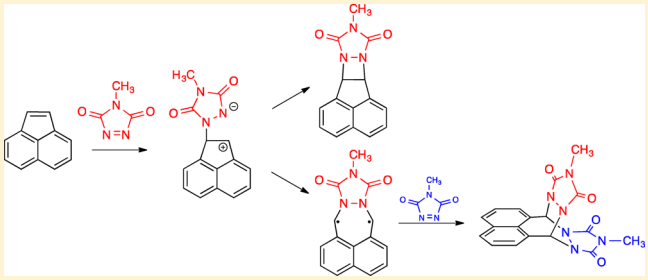
Supporting Information

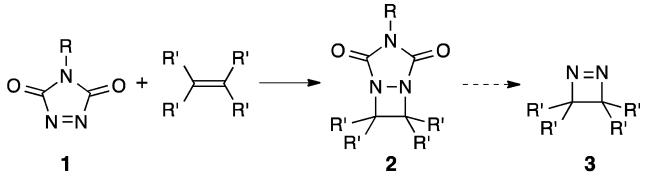
ABSTRACT: The reaction of *N*-methyl-1,2,4-triazoline-3,5-dione (MeTAD) with acenaphthylene and indene leads not only to the formation of the expected [2 + 2] diazetidine cycloadducts but also to unexpected 2:1 adducts of MeTAD with substrate. The structures of the products derived from acenaphthylene were confirmed by X-ray crystallography. A similar distribution of products was afforded from indene. The 2:1 adducts appear to derive from a diradical intermediate, the radical centers of which are strongly stabilized by the bridging urazoyl ring and benzylic delocalization. The triplet states of these diradical intermediates may be trapped via exposure to molecular oxygen to afford oxygen-containing adducts. Computational studies at the (U)B3LYP/6-31G* level provide additional support for the conclusions of our experimental work.



INTRODUCTION

1,2,4-Triazoline-3,5-diones (**1** in Scheme 1) are powerful azo electrophiles.[1] They are known to engage in a variety of thermal and photochemical reactions with alkenes and aromatic compounds, including ene reactions, aromatic substitutions, Diels–Alder cycloadditions, and [2 + 2] cycloadditions.[1] The [2 + 2] cycloaddition leads to a class of strained 1,2-dinitrogen cyclobutane heterocycles known as diazetidines (**2**; Scheme 1).[2−4] Diazetidines have long been of interest because of their structural resemblance to dioxetanes,[2] their potential aromatic characteristics (for 3,4-unsaturated derivatives),[3] and their ready conversion to another class of interesting molecules, the strained four-membered-ring azo compounds known as diazetines (**3**; Scheme 1).[4]

Scheme 1. [2 + 2] Reaction of Triazolinediones (1) with Alkenes To Form Diazetidines (2) and Their Conversion to Diazetines (3)



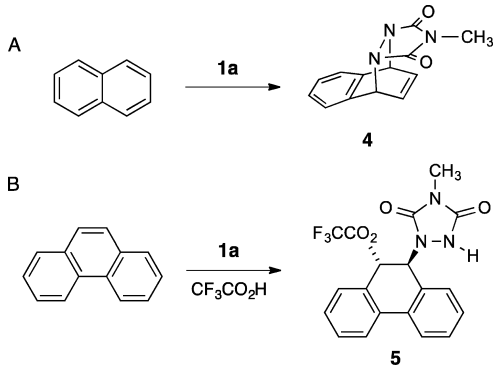
1
a R = Me
b R = Ph

2

3

Several years ago we reported on the thermal reaction of *N*-methyl-1,2,4-triazoline-3,5-diones (**1a**, MeTAD) with naphthalene (as well as substituted naphthalenes) to afford the Diels–Alder cycloadduct **4** (Scheme 2A).[5] Phenanthrene, which can be considered to be a benzannulated naphthalene, resisted reaction with **1a** despite the known tendency of phenanthrene to react with some electrophiles across the 9,10-positions.[6] In the presence of trifluoroacetic acid, however, we found that addition occurred readily to afford the substituted urazole **5** (Scheme 2B).[6] Acenaphthylene (**6**) has structural characteristics in common with both naphthalene and phenanthrene, including the napthyl core as well as an electrophile-reactive C=C bond (i.e., at the 1,2-position). Therefore, the investigation of the reaction of **1a** with **6** seemed like a logical extension of these earlier studies. The reaction was found to take place readily between these two compounds, but at least

Scheme 2. Thermal Reactions of MeTAD (1a) with Naphthalene (A) and Phenanthrene (B)



4

5

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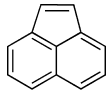
one of the products isolated was quite unexpected. Herein, we describe the results of these studies.



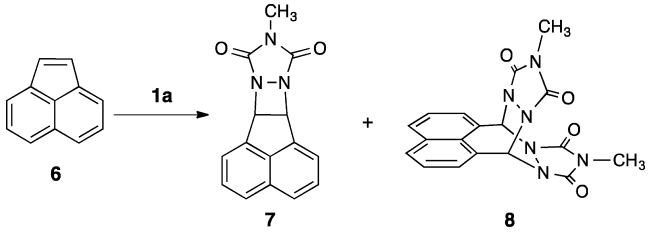
6

RESULTS AND DISCUSSION

Reaction of MeTAD (1a) with Acenaphthylene (6). Addition of a pinkish red CH_2Cl_2 solution of **1a** to 1 equiv of **6** in the same solvent resulted in rapid formation of a deep blood red solution. A similar coloration had been previously observed from formation of charge-transfer complexes between **1a** and electron-rich aromatics.[5,7] Over the course of 1 h the color gradually lightened, ultimately giving rise to an orange-red solution whose appearance did not change further. Thin-layer chromatography demonstrated that **1a** had been completely consumed. Two products were formed in low yield (12% total) in addition to an orange-red polymeric material. Similar amorphous polymeric byproducts have been observed before in TAD reactions and they were, therefore, not further investigated.[8] The two products were separated and purified via column chromatography. Unreacted **6** (42%) was also isolated.

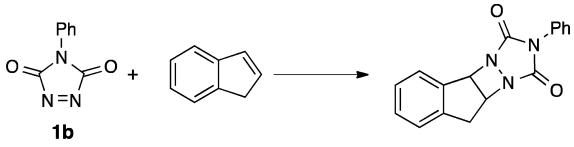
The less polar compound by TLC, formed in a mere 5% yield, proved to be a [2 + 2] cycloadduct, **7** (Scheme 3).

Scheme 3. Products from the Reaction of MeTAD (1a) with Acenaphthylene (6)



Formation of this product is analogous to the well-known [2 + 2] reaction of *N*-phenyl-1,2,4-triazoline-3,5-dione (**1b**, PhTAD) with indene (Scheme 4).[8c] The ^{1}H NMR spectrum of **7** exhibited, in addition to the expected six aromatic protons, a sharp singlet at 6.18 ppm for the benzylic diazetidine protons and a broadened singlet at 2.68 ppm for the *N*-Me protons. Broadening of the signal for the *N*-Me group is likely due to slow double-nitrogen inversion of the urazole ring.[9] This was corroborated by heating a sample of **7** in $CDCl_3$ to 60 °C in the probe of the NMR spectrometer, which led to significant sharpening of the *N*-Me signal without affecting the remaining signals. X-ray crystallography confirmed the assignment of the structure as a [2 + 2] cycloadduct (Figure 1).

Scheme 4. Diazetidine Product from the [2 + 2] Reaction of PhTAD (1b) with Indene



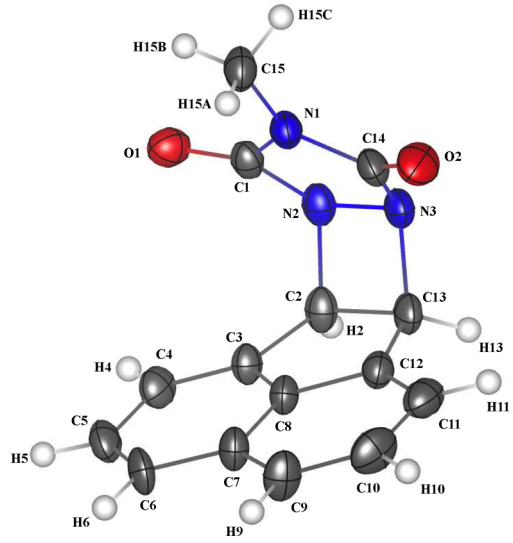


Figure 1. Single-crystal X-ray crystallographic structure of compound **7**.

The ^{1}H NMR spectrum of the second product isolated (7% yield) revealed six aromatic protons for the naphthyl ring, two protons for a singlet representing the benzylic hydrogens, and six protons for an *N*-Me singlet. The spectrum, therefore, was consistent with a 2:1 adduct between **1a** and **6**, respectively. Furthermore, close examination of the ^{13}C satellite signals for the singlet of the benzylic protons revealed them to be sharp singlets. If the C−C σ bond were intact, these signals should appear as doublets due to vicinal coupling, as they do for compound **7** (J = 5 Hz) (where the σ bond is intact). These observations, in addition to the C_s symmetry of the compound apparent from the ^{13}C NMR spectrum (total of nine signals), suggested formation of the 2:1 adduct **8** (Scheme 3). The proposed structure of **8** was subsequently confirmed by X-ray crystallography (Figure 2).

Dougherty reported that reaction of **1a** with bicyclobutane led to a cycloadduct in which **1a** added across the molecule's strained C−C σ bond (Scheme 5).[8a] In addition to formation of the adduct, a polymeric product was formed, similar to what we observed in the reaction of **1a** with **6**. He further determined that less polymerization was observed, and greater yields of cycloadduct realized, when the reaction was conducted in the nonpolar solvent hexane rather than more polar solvents (e.g., CH_2Cl_2, acetone, etc.).[8a] We therefore repeated the reaction between **1a** and **6** in two nonpolar solvents, benzene and hexane. Reaction in benzene afforded results comparable to that of reaction in CH_2Cl_2, and a 5% yield of **7** and 10% yield of **8** were obtained. Compound **1a** has very low solubility in hexane; therefore, larger volumes of solvent (200 mL of hexanes versus 5 mL of CH_2Cl_2) were required for the reaction. The reaction was exceptionally slow in hexane at room temperature, but at reflux temperatures reaction took place over 5 h. As foretold by Dougherty's results, increased yields of **7** (21%) and **8** (17%) were indeed observed. This significant difference in yields is not attributable solely to the change in starting concentrations, since when a similar reaction was conducted in 200 mL of CH_2Cl_2, formation of neither **7** nor **8** was observed. Apparently, under these conditions, all reactivity was funneled into formation of the polymeric product.

While formation of the [2 + 2] cycloadduct **7** was unsurprising, on the basis of the known reactivity of

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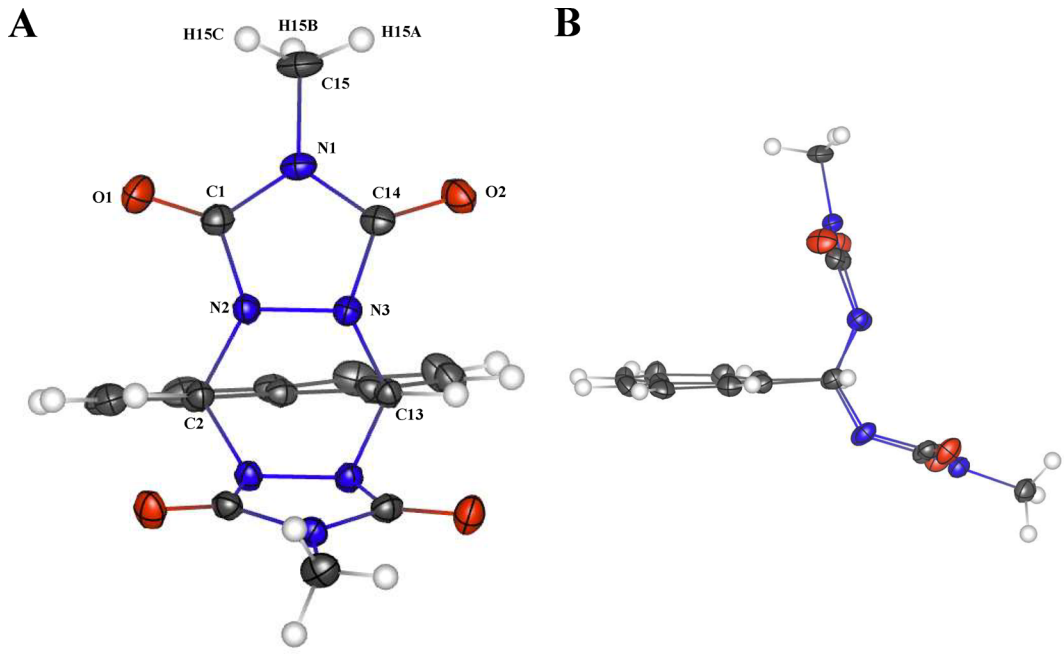
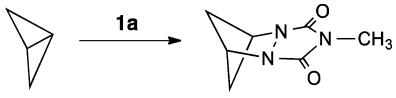


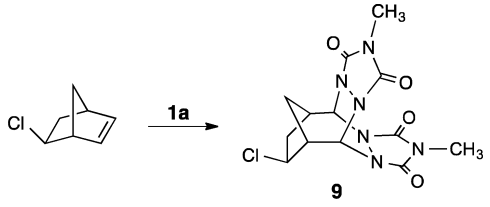
Figure 2. Single-crystal X-ray crystallographic structure of compound **8** as viewed from the front (A, naphthyl rings toward the back) and the side (B) of the molecule.

Scheme 5. Reaction of MeTAD (1a) with the Strained σ Bond of Bicyclobutane



triazolinediones with indene and other appropriately substituted alkenes,[1,8c] formation of the 2:1 adduct **8** was quite unexpected, and its mechanism of formation was not obvious. We were able to locate only one other instance in which thermal reaction of **1a** with a C=C bond resulted in cleavage of both the π and σ bonds. Adam reported that, during the reaction of **1a** with 4-chloronorbornene, the 2:1 cycloadduct **9** was isolated in 10% yield (Scheme 6).[2b] Interestingly, in that paper the authors noted that (at least up to that time) there had been neither "analogy nor precedence in TAD chemistry" for such reactivity.

Scheme 6. Reaction of MeTAD (1a) with 5-Chloronorbornene



9

Possible Nature of a Reaction Intermediate. As mentioned earlier, triazolinediones are known to add across some strained C–C σ bonds, including those of bicyclobutanes, bicyclopentane, and naphthocyclopropene (e.g., Scheme 5).[8a,10] It appeared reasonable, therefore, that reaction of **1a** across the potentially strained σ bond of **7** might be the source of adduct **8**. However, treatment of **7** in $CDCl_3$ with 1 equiv of **1a** failed to yield any **8** even over several days of monitoring by ^{1}H NMR spectroscopy. However, heating a sealed equimolar $CDCl_3$ solution of **7** and **1a** in an NMR tube at 100 °C resulted in slow loss of **7**, as determined by periodic observation by ^{1}H NMR spectroscopy. In addition to formation of a large number of decomposition products (presumably deriving from both **7** and **1a**), signals corresponding to compound **8** eventually appeared and slowly increased in intensity. After 48 h, separation of the reaction mixture by column chromatography afforded **8** in 16% yield along with recovered **7** (29%). One conceivable route for formation of **8** under these conditions is a retro-[2 + 2] cycloaddition of **7** to form **1a** and **6**, followed by the forward reaction of **1a** and **6** to afford **7** and **8**. However, no traces of **6** were detected in the crude reaction mixture by either ^{1}H NMR spectroscopy or TLC analysis. Given that in other reactions between **1a** and **6** approximately 40% of starting **6** was recovered, it is probable that at least some of the generated **6** from a retro-cycloaddition would remain unreacted. Therefore, it seems more likely that, under these conditions, **8** is formed either by direct reaction of **1a** with **7** or by reaction of **1a** with a reactive intermediate generated from **7** (see below).

Reaction products similar in structure to **8** have been previously reported by Arnold (e.g., **13** in Scheme 7).[11] These compounds were generated by trapping diradicals of type **11** by **1b**, which in turn were generated by elimination of N_2 from precursor azo compounds of type **10**. For some derivatives it was determined that diradical species **11** and ring-closed diazetidine **12** were apparently able to exist in equilibrium in solution (Scheme 7).[11b] Additional experimental and computational studies by Abe demonstrated that the urazoyl moiety is highly effective at stabilizing both singlet and triplet state diradicals of this type.[12] In some cases the triplet state was even found to be the ground state for such diradicals.[12]

It appeared plausible, therefore, that a similar diradical reaction intermediate **14**, formed during the reaction of **1a** with **6**, could be responsible for the formation of **8** (Scheme 8). In addition to stabilization of the radical sites by the urazole ring,

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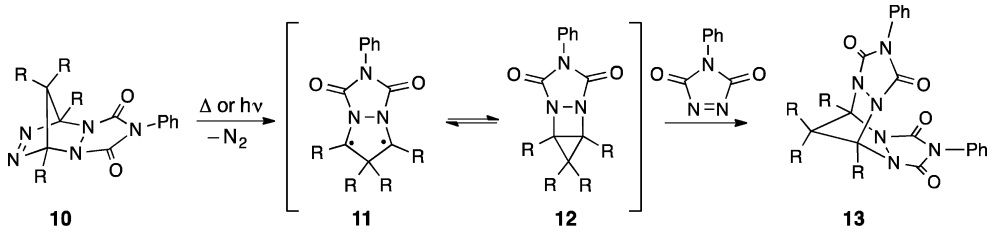
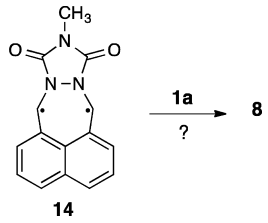
Scheme 7. PhTAD-Trapped 1,3-Diradical Intermediates



Scheme 8. Possible Route to the Formation of 8 via the Intermediacy of Diradical 14



additional stabilization would be expected from resonance interactions of the unpaired electrons with the aromatic ring as a result of being positioned at benzylic positions. We conducted calculations on the postulated diradical intermediate **14** at the DFT UB3LYP/6-31G* level. This level of theory has been previously demonstrated by Abe to be effective at predicting the relative energies of singlet and triplet ground states for dinitrogen-bridged diradicals at relatively low computational cost.[12b] The singlet state diradical species of **14** was calculated to be planar with C_s symmetry and had a zero-point corrected energy of −892.64807 hartree and $\langle S^2 \rangle$ = 0.8678 (Figure 3A).

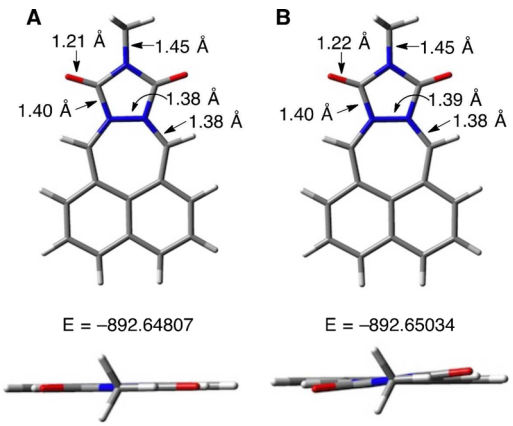


Figure 3. Predicted structures for singlet state **14** (A) and triplet state **14** (B) computed at the UB3LYP/6-31G* level. Some relevant bond lengths are provided for comparison. Below each is the identical structure viewed down the N−CH_3 bond. The planar structure of singlet **14** and the puckered structure of triplet **14** may be readily observed. Zero-point corrected energies are in hartrees.

The optimized structure for the triplet state of diradical **14**, however, was nonplanar (the two nitrogen atoms being slightly pyramidalized in opposite directions and on opposite sides of the plane defined by the aromatic rings) with a zero-point corrected energy of −892.65034 hartree and $\langle S^2 \rangle$ = 2.0748 (Figure 3B). Thus, the triplet state is predicted to be the ground state for this diradical by 2.4 kcal/mol (after correction for spin contamination using Yamaguchi's method).[13] This S-T energy gap is comparable to that (+1.5 kcal/mol) calculated for a similar urazole-bridged diradical reported by Abe.[12b] With the exception of the difference in planarity versus nonplanarity, however, the salient bond lengths (e.g., N−N, HC−N, C═O) for the two structures were nearly identical to within ±0.01 Å (see Figure 3). Unlike Arnold's compounds, however, diazetidine **7** is apparently not in equilibrium with diradical **14**, since **7** failed to react with **1a** in solution at room temperature as described earlier. We sought to support this conclusion with additional computational studies.

At the DFT B3LYP/6-31G* level we found minima for both *endo* and *exo* conformers of diazetidine **7** (**7**-*endo* and **7**-*exo*, respectively; Figure 4). The two conformers were nearly identical in energy with only a slight preference for the *endo* isomer (by ∼0.1 kcal/mol). This is consistent with the X-ray crystal structure for **7**, which exhibited the urazole ring locked in the *endo* position (see Figure 1), although the effects of crystal packing may well be responsible for this observation. The C−N (1.51 Å), N−N (1.45 Å), and C−C (1.57 Å) bond lengths computed for the **7**-*endo* structure correlated well with the values obtained from the crystal structure (1.52, 1.46, and 1.56 Å, respectively). Additionally, the degree of pyramidalization of the diazetidine nitrogen atoms as measured by the average of the three bond angles (α_{av}) for the calculated structure (108.0°) was fairly close to that measured from the crystal structure (107.2°). Employing the UB3LYP functional, we were able to locate a transition state structure (**15**) linking the **7**-*exo* compound with singlet diradical **14** (Figure 4). The identity of the calculated transition state structure was confirmed by frequency and IRC calculations. The difference in energies between **7**-*exo* and the transition state **15** (+31.8 kcal/mol) is quite substantial. Therefore, the ring opening of **7** to **14** is not a likely process at room temperature. However, at higher temperatures (e.g., 100 °C as discussed above) the ring-opening process becomes more feasible. Therefore, the previously described observation that the 2:1 adduct **8** was formed when a solution of **7** was heated in the presence of **1a** may be explained by trapping of diradical intermediate **14** (generated by ring opening of **7**) by **1a**.

We considered the possibility that singlet diradical **14** could be the precursor to both diazetidine **7** (by ring closure (ΔE_{calc}(**14**→**15**) = +18.7 kcal/mol)) and 2:1 adduct **8** (by trapping of **14** by **1a**). In an attempt to limit the amount of freely available **1a** and thereby hinder formation of **8**, we conducted a reaction in which a solution of 1 equiv of **1a** in CH_2Cl_2 (3 mL) was added in regular portions to a refluxing solution of **6** in hexane (200 mL) over the course of 3.5 h. If **14** indeed leads to the formation of both **7** and **8**, under these reaction conditions we might expect to observe an increase in the yield of **7** and a decrease in the yield of **8**. Interestingly, however, results nearly identical with those obtained when both

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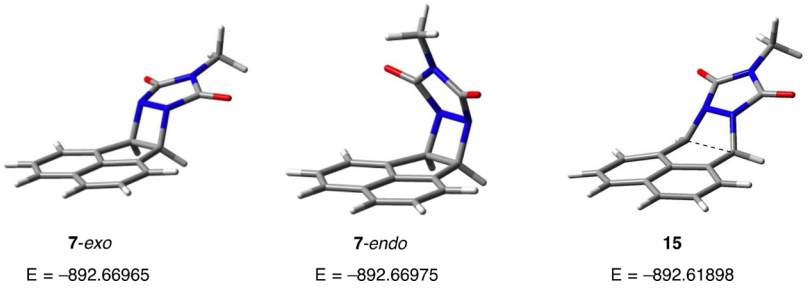


Figure 4. Predicted structures for 7-*exo*, 7-*endo*, and transition state **15** computed at the (U)B3LYP/6-31G* level. Zero-point corrected energies are in hartrees.

1a and **6** were present at the outset were observed (i.e., a 24% yield of **7** and an 18% yield of **8**).

Triplet diradicals are known to be reactive with molecular oxygen.[14] To test whether the triplet state of diradical **14** was populated as suggested by the DFT calculations, we conducted a reaction in benzene as solvent in which equimolar amounts of **1a** and **6** were allowed to react amidst a continuous fine stream of introduced oxygen gas. The percent yields of both **7** (3%) and **8** (9%) were hardly affected relative to the reaction in the absence of oxygen, but a new compound was formed in 18% yield. Integrations of the relevant signals in the ^{1}H NMR spectrum suggested that this product was formed from 1 equiv each of **1** and **6**. Again, the ^{13}C satellites of the benzylic protons were observed to be singlets, heralding the absence of a connecting σ bond between the two carbons. HRMS analysis confirmed the presence of an additional oxygen atom in the structure. Finally, X-ray crystallography confirmed the structure as that of compound **16** (Figures 5 and 6). While the formation

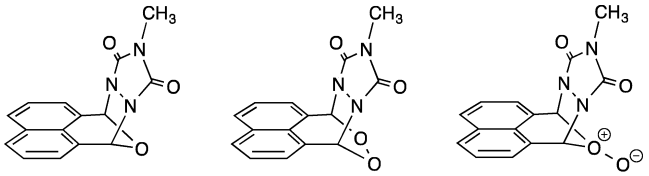


Figure 5. Compound **16** formed from the reaction of **1** and **6** in the presence of O_2, along with possible precursor compounds **17** and **18**.

of **16** is consistent with the trapping of a triplet diradical intermediate, its ultimate mechanism of formation remains a mystery at this point. It presumably derives from further reaction of either an initially formed cyclic peroxide **17** or possibly a peroxonium ion of type **18**, both of which are reasonable initial products of reaction between triplet **14** and O_2 (Figure 5).

In an attempt to trap diradical intermediate **14** by an alternative electrophile, we conducted the reaction of **1a** with **6** in the presence of 1 equiv of DEAD. A control experiment showed little or no reaction between DEAD and acenaphthylene over the time required for complete consumption of **1a**. Unfortunately, however, no products other than **7** and **8** were observed by TLC and ^{1}H NMR analysis of the crude reaction mixture.

Reaction of MeTAD (1a) with Indene. Indene is structurally similar to **6**, but it lacks the second fused benzene ring. The reaction between PhTAD and indene to undergo a net [2 + 2] cycloaddition to form a diazetidine has been known for a long time (see Scheme 4).[8c] The reaction has been studied

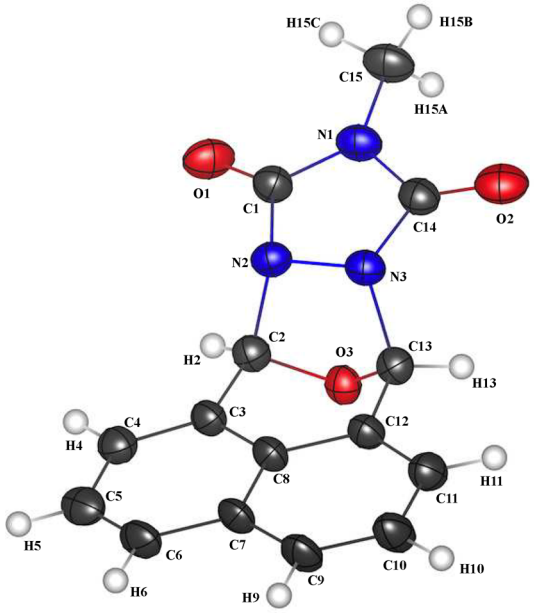
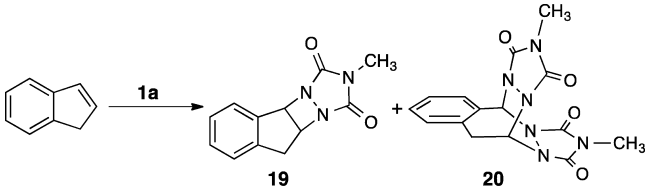


Figure 6. Single-crystal X-ray crystallographic structure of compound **16**.

in greater detail since the original report.[2a,15] No products other than the diazetidine have been reported from these reactions. However, we could find no account in which MeTAD (**1a**) rather than PhTAD (**1b**) was utilized. Therefore, we allowed **1a** to react with indene in benzene as solvent and, as in the reaction with **6**, isolated two major products. The first product was the expected [2 + 2] diazetidine **19** (10% yield) in analogy to the reaction with PhTAD (see Scheme 9). Integration of the

Scheme 9. Reaction of MeTAD (1a) with Indene



signals in the ^{1}H NMR spectrum of the second product, like the 2:1 adduct **8** from **6**, suggested a 2:1 addition product of **1a** to indene. Similarly as well, the spectrum failed to show coupling between the two methine protons. The benzylic bridgehead proton appeared as a singlet at 6.94 ppm and the other bridgehead proton as a triplet (J = 3.5 Hz) at 6.64 ppm due to

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coupling with the methylene protons. This compound has been assigned structure **20**.

Formation of **20** suggests that an intermediate diradical similar to **14** may form under these conditions. DFT calculations provided puckered structures for both the singlet and triplet optimized diradicals **21** (Figure 7). In this case, the

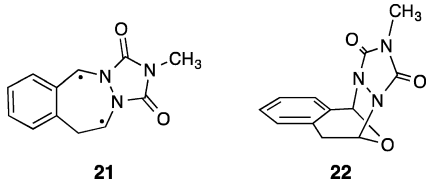

Figure 7. Diradical **21** and its oxygen-trapped product, **22**.

singlet diradical was predicted to be slightly more stable than the triplet state by just 0.1 kcal/mol (after correcting for spin contamination). Consistent with thermal accessibility of the triplet state of **21** was the observation that when the reaction was conducted in oxygen-saturated benzene in the same manner as the reaction of **1a** with **6** described earlier, a new product, assigned structure **22**, was observed in low yield (2%).

Postulation of a Reaction Mechanism on the Basis of Experimental and Computational Findings. The mechanism of TAD reactions with alkenes remains a subject of debate. Early studies suggested the intermediacy of aziridinium imides (AI; Figure 8).[16] Later studies, however, suggested that

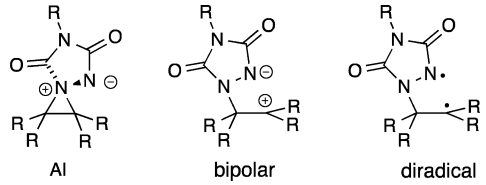

Figure 8. Possible intermediates formed during the reaction of TADs with alkene substrates.

AIs are not actual precursors to products, dismissing them as "innocent bystanders" in the reactions as opposed to being "perpetrators".[16,17] Instead, observed products were suggested to form from ring-opened species of either a bipolar and/or diradical nature (Figure 8).[16−18]

Computational studies on our system confirmed the relative energies of the ring-opened species versus the AIs. Two AI structures, **23a**,**b**, were located as energy minima (Figure 9). AI **23a** has the urazole ring oriented "inward" relative to the acenaphthylene ring, while **23b**'s urazole ring is oriented away from the acenaphthylene ring. Both structures sport C_s symmetry. AI **23a** is predicted to be 2.3 kcal/mol more stable than **23b**. The ring-opened intermediate **24** was optimized at the RB3LYP/6-31G* level (E = −892.630886) and then the energy recalculated as a singlet diradical employing UB3LYP/6-31G* (E = −892.637659). The diradical structure was found to be 4.2 kcal/mol more stable than the zwitterionic structure, but this ordering could potentially be reversed in the presence of solvation effects.[17b,18a] Furthermore, ring-opened **24** was 5.2 kcal/mol more stable than the AI intermediate **23a**. A transition state structure, **25**, was located that connected AI **23a** with ring-opened **24** with a mere difference in energy between **24** and transition state **25** of 7.0 kcal/mol, suggesting ready conversion between the two intermediates **23a** and **24**.

AI and bipolar intermediates have been successfully trapped in some cases when a TAD reaction is carried out in the presence of methanol.[2a,15,16,17b,18b,c] Generally these types of reactions are carried out at low temperatures, since TADs are reactive with alcohols.[19] Therefore, we conducted the reaction of **1a** and **6** in a 3:1 mixture of CH_2Cl_2 and MeOH at −20 °C. Compound **1a** was completely consumed within 2 h to afford a yellow-orange solution. Examination of the crude reaction mixture by TLC and ^{1}H NMR failed to show the presence of any products (including **7** and **8**) other than what appeared to be a series of decomposition products from **1a**. The starting **6** remained untouched. Apparently the reaction of **1a** with MeOH is faster than the reaction of **1a** with **6** under these conditions.

Since it has been established that the proposed intermediate diradical **14** does not form spontaneously from adduct **7** at room temperature, it must necessarily be generated during formation of the second C−N bond from either intermediate **23** or **24**. The fact that nearly identical results were obtained from the refluxing hexane reactions in which **1a** was added in portions to **6** versus the reaction where both **1a** and **6** were present at the outset of the reaction suggests that the formations of **7** and **8** are not in competition. If they were in competition, more **7** and less **8** should have been observed from the portionwise addition reaction, since less **1a** would have been present to trap **14** and afford **8**. We suggest that, during formation of the second C−N bond, a divergence occurs in which one pathway (a, in Scheme 10) leads to the [2 + 2] adduct **7**, and a second pathway (b, in Scheme 10) results in C−C bond cleavage to form diradical intermediate **14**. Diradical **14** must have a sufficient lifetime to allow for reaction with **1a**, even when the concentration of **1a** is relatively low. Triazolinediones are known to be effective radical

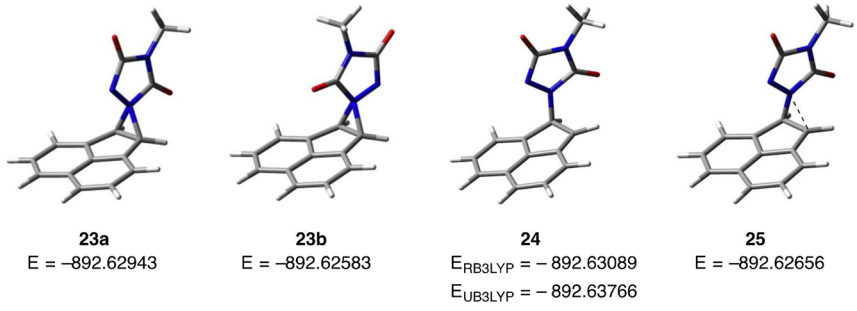

Figure 9. Predicted aziridinium imide and ring-opened intermediates, and the transition state structure (**25**) linking **23a** with **24**, computed at the (U)B3LYP/6-31G* level. Zero-point corrected energies are in hartrees.

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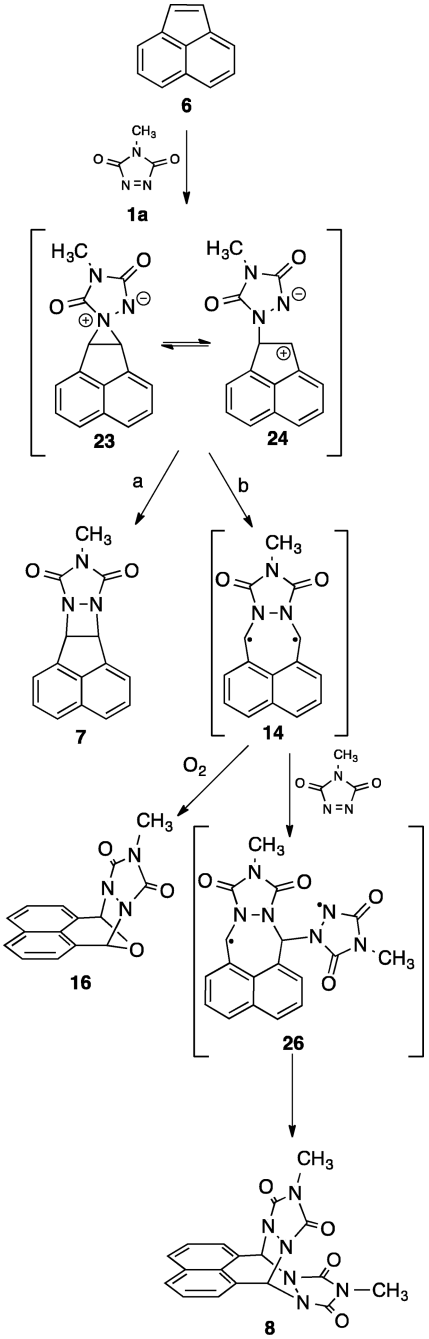
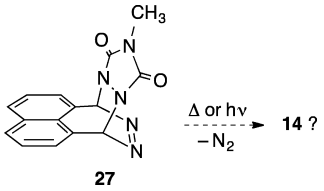
Scheme 10. Proposed Reaction Mechanism for the Reaction of MeTAD (1a) with Acenaphthylene (6)



acceptors;[20] therefore, trapping of **14** by **1a** to form diradical intermediate **26** followed by ring closure to afford observed adduct **8** is reasonable (Scheme 10). Whether reaction of **14** with **1a** is possible from both the singlet and triplet states of **14**, or whether only one spin state is responsible, is unknown at this point. We intend to investigate this further with future studies (see below). Successful trapping of **14** by oxygen to ultimately afford **16**, however, does confirm population of a triplet diradical species.

We hope to gain better insight into the nature and reactivity of the proposed diradical intermediate **14** by attempting its generation via an independent route (Scheme 11). We are currently working on the synthesis of compound **27**, which upon liberation of N_2 either thermally or photochemically should yield **14** directly.

Scheme 11. Possible Generation of Diradical 14 via Thermal and/or Photochemical Elimination of N_2 from 27



CONCLUSIONS

Despite a long history of investigations into the reactivity of the potent electrophile MeTAD (**1a**), it continues to provide unexpected and fascinating results. The reaction of **1a** with both **6** and indene was expected to take place via previously precedented net [2 + 2] cycloadditions to afford the corresponding diazetidines. In both cases, however, in addition to the expected π bond cleavage to form diazetidines, σ bond cleavage also took place, apparently giving rise to diradical intermediates. Both singlet and triplet states of the diradical intermediates appear to be populated. The diradical intermediates led to the formation of TAD-trapped products **8** (from **6**) and **20** (from indene). The triplet states of both diradicals could be trapped with molecular oxygen. The diazetidine products **7** (from **6**) and **19** (from indene) appear to arise from direct ring closure of either AI intermediates or ring-opened species of either a bipolar or diradical nature.

EXPERIMENTAL SECTION

General Methods. Column chromatography was conducted on silica gel (234−400 mesh) using compound-appropriate mixtures of hexanes and EtOAc as eluent. Thin-layer chromatography was performed on precoated silica gel plates (250 mm) and visualized by ultraviolet light and/or by staining with iodine vapor. ^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz NMR spectrometer. Chemical shifts are reported in units of parts per million downfield from TMS. High-resolution mass spectra (HRMS) were acquired on a MALDI-TOF spectrometer in positive mode. *N*-Methyl-1,3,5-triazoline-3,5-dione (**2**) was synthesized via oxidation of commercially obtained *N*-methylurazole with N_2O_4 according to the literature and sublimed before use.[21] All other chemicals and solvents were obtained from commercial sources and used without further purification.

Reaction of MeTAD (1a) with Acenaphthylene (6) in CH_2Cl_2. To a stirred solution of 250 mg (1.64 mmol) of acenaphthylene (**6**) in 2 mL of CH_2Cl_2, protected from light, was added a solution of 185 mg (1.64 mmol) MeTAD (**1a**) in 3 mL of CH_2Cl_2 via pipet. The resulting blood red solution was stirred until TLC revealed complete consumption of **1a**. The orange solution was concentrated and subjected to column chromatography (50/50 ethyl acetate/hexanes). Compound **7**, 20.2 mg (5% yield), was obtained as a white solid, mp >170 °C (decomposes without melting to black solid): ^{1}H NMR ($CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 6.9 Hz, 2H), 7.64 (dd, J = 6.9, 8.0 Hz, 2H), 6.18 (s, 2H), 2.68 (br s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.9, 140.6, 134.5, 131.8, 128.4, 126.5, 123.5, 70.4, 25.8; HRMS (MALDI) m/z $[M + H]^+$ calcd for $C_{15}H_{12}N_3O_2$ 266.0924; found 266.0921. Compound **8**, 40.7 mg (7% yield), was obtained as a crystalline white solid, mp >250 °C (decomposes without melting to black solid): ^{1}H NMR ($CDCl_3$) δ 7.97 (dd, J = 1.0, 8.3 Hz, 2H), 7.70 (dd, J = 1.0, 6.8 Hz, 2H), 7.58 (dd, J = 6.8, 8.3 Hz, 2H), 7.17 (s, 2H), 3.03 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 152.7, 135.1, 130.9, 129.9, 127.9, 127.5, 126.6, 68.2, 26.1; HRMS (MALDI) m/z $[M + H]^+$ calcd for

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$C_{18}H_{15}N_6O_4$: 379.1149, found 379.1149. Also isolated was 104 mg of **6** (42% recovery).

Reaction of MeTAD (1a) with Acenaphthylene (6) in Benzene. To a stirred solution of 266 mg (1.75 mmol) of **6** in 20 mL of benzene, protected from light, was added a solution of 198 mg (1.75 mmol) of MeTAD (**1a**) in 2 mL of benzene via pipet. The resulting blood red solution was stirred overnight, after which TLC revealed complete consumption of **1a**. The orange solution was concentrated and subjected to column chromatography (50/50 ethyl acetate/hexanes) to afford 20.5 mg (4% yield) of **7** and 66.2 mg (10% yield) of **8**.

Reaction of MeTAD (1a) with Acenaphthylene (6) in the Presence of Oxygen. A solution of 266 mg (1.75 mmol) of **6** in 20 mL of benzene, protected from light, was saturated with oxygen by running a fine stream of oxygen gas through the solution using a sparger. A solution of 198 mg (1.75 mmol) of **1a** was then added via pipet, and the mixture was stirred overnight while the introduction of oxygen continued. TLC revealed complete consumption of **1a**. The orange solution was concentrated and subjected to column chromatography (50/50 ethyl acetate/hexanes) to afford 13.3 mg (3% yield) of **7**, 56.0 mg (9% yield) of **8**, and 87.5 mg (18% yield) of **16** as a white solid. Data for **16**: ^{1}H NMR ($CDCl_3$) δ 7.86 (dd, J = 1.8, 7.5 Hz, 2H), 7.47−7.53 (m, 4H), 6.70 (s, 2H), 3.09 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.2, 132.7, 130.0, 129.1, 126.3, 124.3, 122.3, 89.0, 26.4; HRMS (MALDI) m/z $[M + H]^+$ calcd for $C_{15}H_{12}N_3O_3$: 282.0873, found 282.0873.

Heated Reaction of MeTAD (1a) with Acenaphthylene (6) in Hexanes. A solution of 200 mg (1.32 mmol) of **6** in 200 mL of hexanes in a two-necked 250 mL round-bottomed flask fitted with a condenser and drying tube was heated to reflux. A solution of 149 mg (1.32 mmol) of **1a** in 3 mL of CH_2Cl_2 was added via pipet through the available reaction flask neck, which was then stoppered. The reaction mixture was heated until TLC revealed complete consumption of **1a** (5 h). The orange solution was concentrated and subjected to column chromatography (50/50 ethyl acetate/hexanes) to afford 73.4 mg (21% yield) of **7** and 86.9 mg (17% yield) of **8**. Also isolated was 82.7 mg (54% recovery) of **6**.

Reaction of MeTAD (1a) with 7. A solution of 27.3 mg (0.1 mmol) of **7** and 12 mg (0.1 mmol) of **1a** was prepared in 0.5 mL of $CDCl_3$. The red solution was transferred to an NMR tube and the tube sealed with a cap and Parafilm. The contents of the tube were examined periodically using ^{1}H NMR spectroscopy. After 6 days at room temperature there was no sign of reaction. The NMR tube containing the same solution was then cooled in dry ice under vacuum and sealed. The tube was then heated at 100 °C and monitored periodically using ^{1}H NMR spectroscopy. After 48 h, the solution was cooled, the tube was broken, and the contents were concentrated. Column chromatography (50/50 ethyl acetate/hexanes) afforded 8.4 mg (29% recovery) of **7** and 5.8 mg (16% yield) of **8**.

Reaction of MeTAD (1a) with Indene in Benzene. To a stirred solution of 410 mg (3.53 mmol) of indene in 40 mL of benzene, protected from light, was added a solution of 400 mg (3.53 mmol) of MeTAD (**1a**) in 4 mL of benzene via pipet. The resulting blood red solution was stirred overnight, after which TLC revealed complete consumption of **1a**. The orange solution was concentrated and subjected to column chromatography (50/50 ethyl acetate/hexanes) to afford 54.6 mg (7% yield) of **19** as a gummy solid, and 160 mg (13% yield) of **20** as a viscous liquid. Data for **19**: ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 7.7 Hz, 1H), 7.30−7.42 (m, 3H), 5.80 (d, J = 6.0 Hz, 1H), 5.26 (dd, J = 6.0, 6.7 Hz, 1H), 3.75 (d, J = 18.5 Hz, 1H), 3.25 (dd, J = 6.7, 18.5 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 162.7, 142.7, 135.5, 130.8, 128.2, 127.0, 126.0, 73.1, 67.3, 35.7, 26.0; HRMS (MALDI) m/z $[M + H]^+$ calcd for $C_{12}H_{12}N_3O_2$ 230.0924, found 230.0923. Data for **20**: ^{1}H NMR ($CDCl_3$) δ 7.40−7.50 (m, 2H), 7.30−7.37 (m, 2H), 6.94 (s, 1H), 6.64 (t, J = 3.6 Hz, 1H), 3.78 (d, J = 3.6 Hz, 2H), 3.04 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 152.1, 152.0, 131.9, 131.5, 130.7, 130.1, 128.3, 127.4, 66.4, 61.5, 39.5, 25.8; HRMS (MALDI) m/z $[M + H]^+$ calcd for $C_{15}H_{15}N_6O_4$ 343.1149, found 343.1151.

Reaction of MeTAD (1a) with Indene in Benzene in the Presence of Oxygen. A solution of 204 mg (1.75 mmol) of indene in 20 mL of benzene, protected from light, was saturated with oxygen by running a fine stream of oxygen gas through the solution using a sparger. A solution of 198 mg (1.75 mmol) **1a** was then added via pipet, and the mixture was stirred overnight while the introduction of oxygen continued. TLC revealed complete consumption of **1a**. The orange solution was concentrated and subjected to column chromatography (50/50 ethyl acetate/hexanes) to afford 20.0 mg (5% yield) of **19**, 64.5 mg (11% yield) of **20**, and 10.2 mg (2% yield) of **22** as a viscous liquid. Data for **22**: ^{1}H NMR ($CDCl_3$) δ 7.36 (dt, J = 2.0, 7.0 Hz, 1H), 7.24−7.32 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 6.37 (s, 1H), 6.07 (d, J = 4.0 Hz, 1H), 3.41 (dd, J = 4.0, 17.4 Hz, 1H), 3.10 (d, J = 17.4 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.1, 159.7, 133.0, 129.9, 129.2, 129.1, 127.0, 125.1, 88.6, 86.7, 34.0, 26.2; HRMS (MALDI) m/z $[M + H]^+$ calcd for $C_{12}H_{12}N_3O_3$ 246.0873, found 246.0874.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving ^{1}H and ^{13}C NMR spectra for all fully characterized compounds, crystallographic data for **7**, **8**, and **16**, Cartesian coordinates and zero-point corrected energies for all calculated minima, and zero-point corrected energies, spin expectation values, and imaginary frequencies for transition state structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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